INVESTIGATION OF ACCIDENT INVOLVING TITANIUM AND RED FUMING NITRIC ACID, DECEMBER 29, 1953

BY P. M. AMBROSE, J. C. BARRETT, R. W. HUBER, DAVID SCHLAIN, AND V. C. PETERSEN

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P. M. Ambrose,[1] J. C. Barrett,[2] R. W. Huber,[3]
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INTRODUCTION

This report describes an accident, which took place in the Chemical Corrosion Laboratory at the College Park, Md., Station of the Federal Bureau of Mines. The accident occurred while Walter L. Acherman, chemist, was performing a routine manipulation during a corrosion experiment involving commercially pure titanium and red-fuming nitric acid. There was a sudden and very violent reaction, and a large quantity of acid was thrown in the face and over the body of Acherman, causing serious injury. L. B. Golden, chief of the Chemical Corrosion Section, was exposed to nitric acid fumes during the ensuing rescue and first-aid operations and died on January 25, 1954. According to the medical report, the direct cause of Mr. Golden's death was pulmonary edema and confluent bronchopneumonia; the contributary cause was inhalation of fumes from red fuming nitric acid.

The following employees of the College Park Station contributed to this report by supplying information on the accident and assisted in the rescue operation: L. B. Golden, chief, Chemical Corrosion Section; T. E. Green, chemist; Robert Warfield, chemist; L. A. DeVivo, laboratory mechanic; D. W. Chalkley, laboratory mechanic; E. H Neagle, laboratory welder; and R. L. Heath, laboratory general mechanic.

ACKNOWLEDGMENTS

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GENERAL INFORMATION

The Chemical Corrosion Section is part of the Physical Metallurgy Branch, Metallurgical Division, Region VIII, and has as its specific function the study of the chemical corrosion behavior of metals with a view toward evaluating these metals as materials of construction. The emphasis since organization of this group about 8 years ago has been on titanium and zirconium and alloys of these metals. A wide variety of corrosion mediums has been used.

At the time of the accident the Chemical Corrosion Section consisted of L. B. Golden and W. L. Acherman, professional chemists, and two laboratory assistants. The two assistants were on leave when the accident occurred. The laboratory space used for chemical corrosion studies occupies the south central portion of the third floor of the Mill building. The remainder of this floor is used for laboratories by the Analytical Chemistry Unit of the Chemical and Physical Section and for offices (fig. 1). The first and second floors are occupied by the Metals and Alloys and the Welding Sections of the Physical Metallurgy Branch.

DESCRIPTION OF ACCIDENT

At the time of the accident, Acherman was working on a group of corrosion tests involving 118 titanium specimens and approximately 7 liters of red fuming nitric acid. The specimens were in 24 Erlenmeyer flasks equipped with stopcocks. The flasks were placed side by side in 2 heavy pyrex glass trays (18 by 12 by 2-7/8 inches) in a fume

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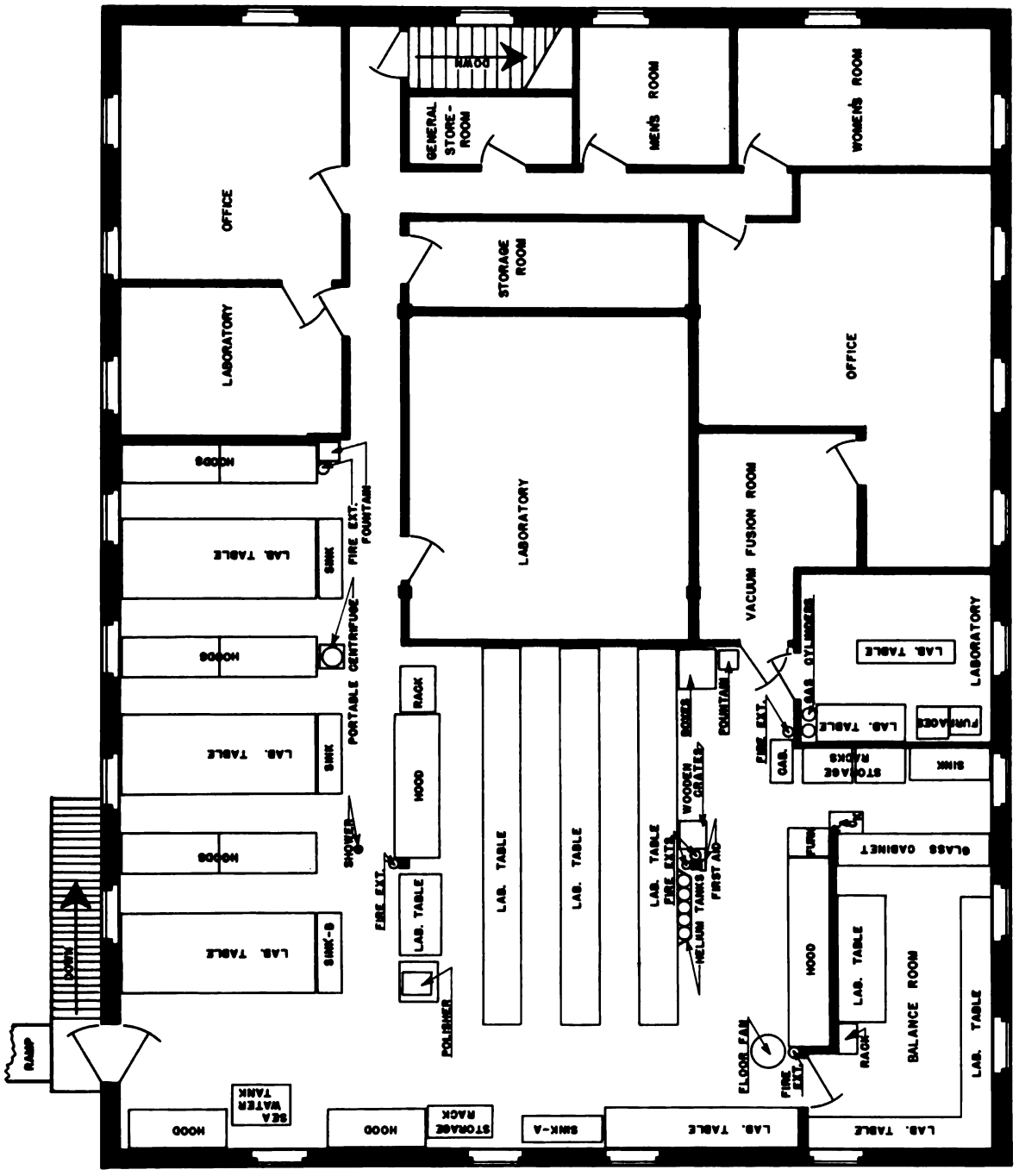

Figure 1. - Drawing of third floor, Mill building.

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hood (figs. 2 and 3). The flasks were never more than one-half inch apart in the trays and in some instances may have been in contact. Although no appreciable pressure was noted, it was routine procedure in these tests to vent the flasks to the atmosphere at 24-hour intervals by means of the stopcocks to make sure that no great pressure buildup would occur. Acherman was engaged in this task when the accident occurred. He was wearing rubber gloves but no goggles. At the beginning of this particular experiment he had worn both of these safety devices but had discontinued the use of goggles after several days during which no unusual pressures were noted in the flasks.

The flasks were in the hood just outside the balance room, adjacent to the floor fan (fig. 1). Apparently Acherman had just touched one of the flasks when a very violent reaction occurred, accompanied by a loud noise, and almost all of the glassware, including the heavy trays, was broken. Acid was thrown over Acherman's face and body, over equipment, and on the floor to a distance of more than 10 feet from the hood opening (figs. 4 and 5). The force generated was sufficient to throw at least 1 specimen, weighing about 8 grams, 20 feet, only a trace of acid was found on the rear face of the hood. The laboratory was quickly filled with heavy brown nitric acid fumes. Acherman was blinded and immediately began to feel intense pain. He managed to reach sink A (left side of room, fig. 1) but was unable to help himself further. He later stated that he fell to the floor before reaching the sink. However, Miss Campbell, the only witness to the accident, stated that she heard a click just before she heard the loud noise and that Acherman staggered back from the hood but did not fall to the floor. This discrepancy may arise from the fact that Acherman, in moving back from the hood opening, came in contact with the bench located in front of the hood, wet his elbows with the acid just thrown there by the reaction and received the impression of being on the floor. Persons who heard the noise of the accident compared the sound to a muffled thud, to the breaking of a glass tube, or to a shotgun blast. Six men working in nearby laboratories rushed in to render first aid. Two of these led Acherman from sink A (figs. 1, 6, and 7) to the vicinity of sink B and the shower (fig. 1). As the shower chain was pulled off in the excitement, a hose in sink B was used to flush the victim, particularly the eyes and head (fig. 8). A few seconds later a second hose was put into play from an adjacent sink; this was used for flushing the lower half of the victim's body. At 3:58 p.m. Acherman was transported to a local hospital in an ambulance.

While some of the men were attending the victim others were opening the windows of the building, starting the ventilating fans, and bringing in additional fans to clear the atmosphere. Sodium carbonate and sodium bicarbonate were spread over the woodwork to neutralize the acid. There was no fire. During these operations several persons, in addition to L. B. Golden, were exposed to nitric acid fumes by inhalation. At present, however, Golden is the only person definitely known to have been seriously affected by the nitric-acid fumes.

SUMMARY OF CORROSION TESTS IN RED-FUMING NITRIC ACID

Tests Carried out before December 1953

Reports and laboratory records show that the study of the corrosion properties of titanium in red fuming nitric acid hereinafter referred to as RFNA, was initiated in this laboratory in April 1948 and that experiments were carried out on four separate occasions before June 30, 1950. The work was done in loosely covered vessels, usually at room temperature, with acid containing 92 percent nitric acid, 6-1/2 percent NO_2, and 1-1/2 percent water. The titanium specimens were cut from sheet rolled from bars consolidated by powder metallurgy techniques. The sheet contained

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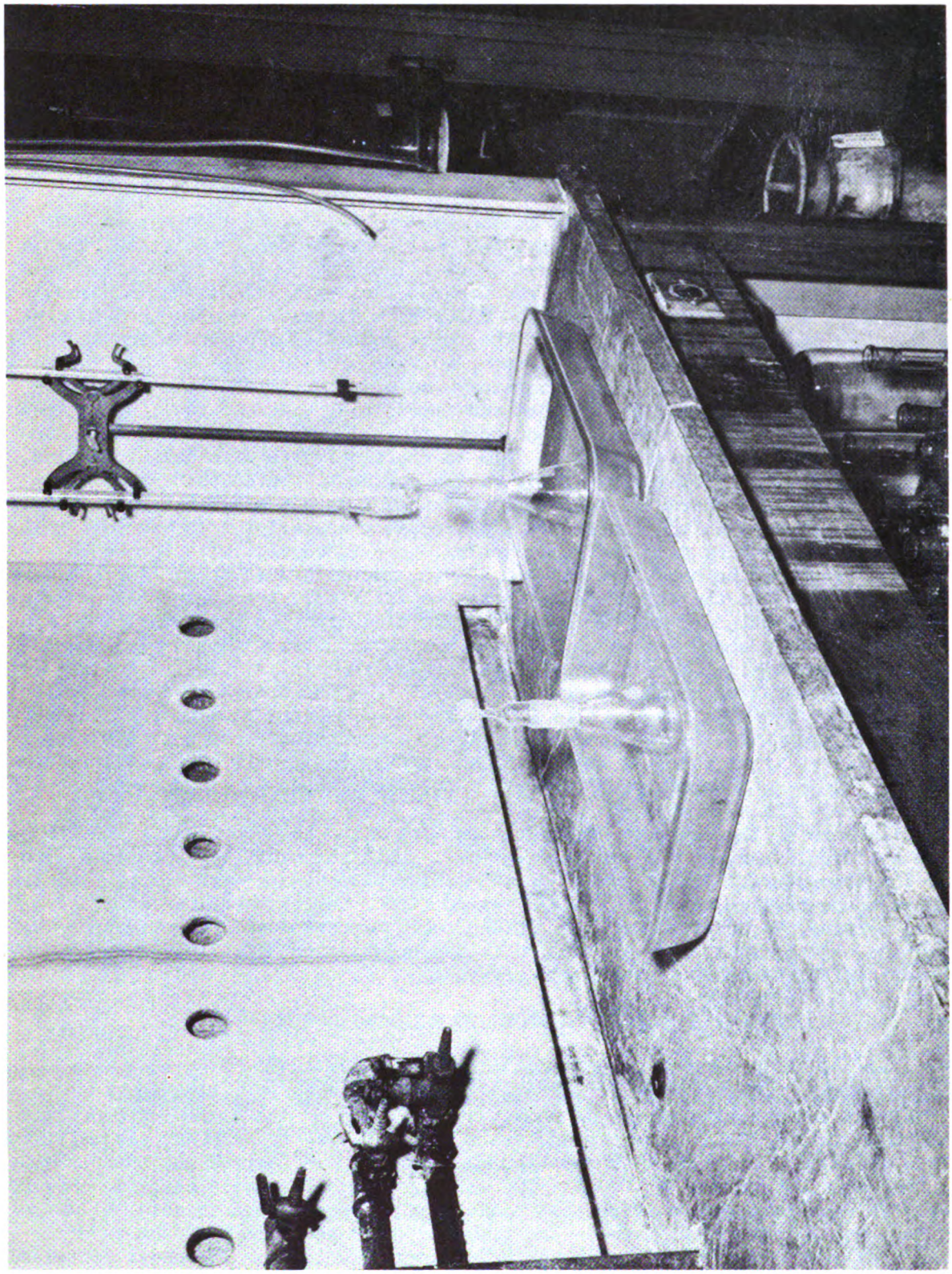

Figure 2. - A closeup view of empty 300 ml. flasks and glass trays in the end of the hood in which the explosion occurred on December 29.

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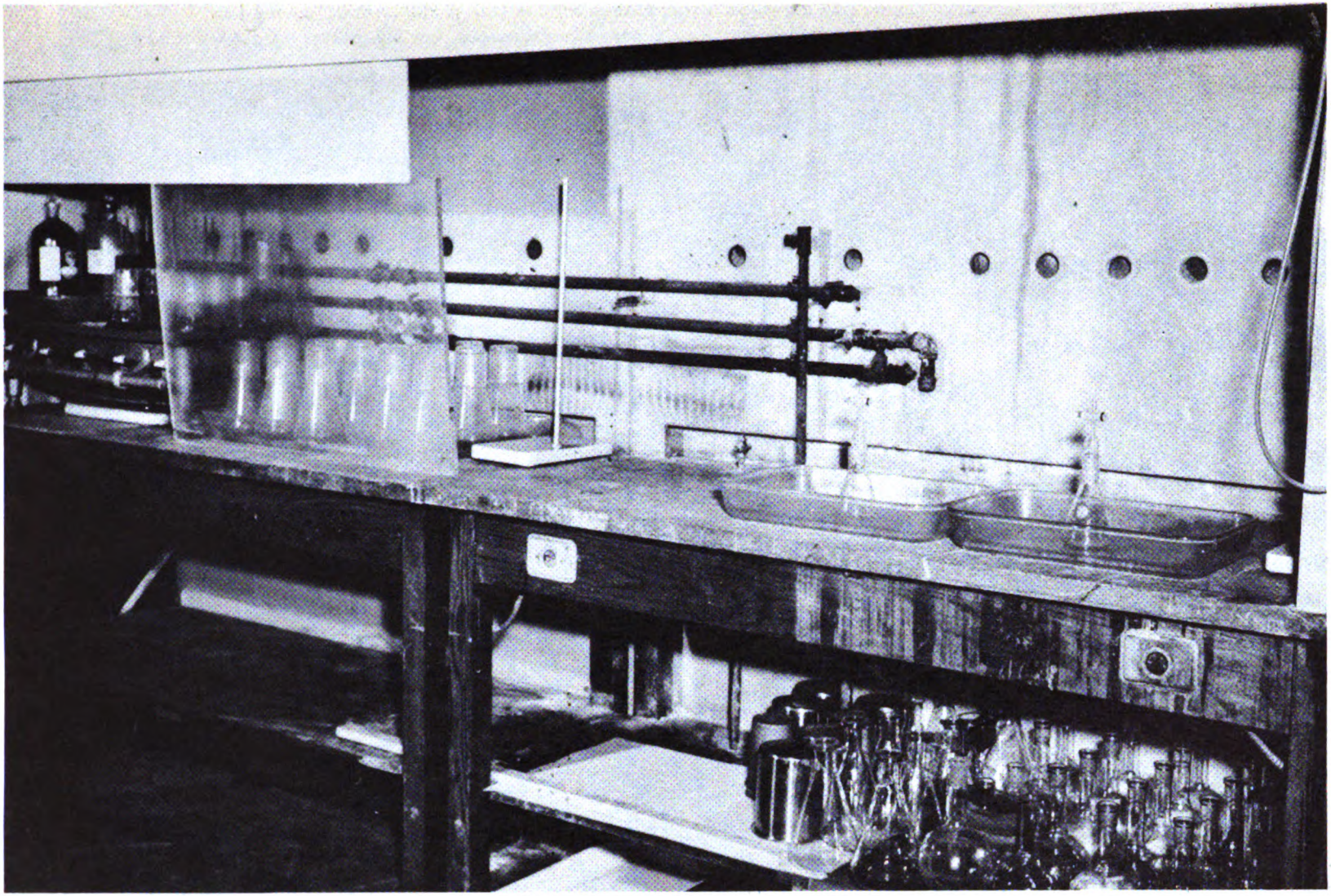

Figure 3. - A view in the southeast corner of the chemical corrosion laboratory, showing an overall view of the hood in which the research on the corrosion of titanium in red-fuming nitric acid was being conducted. This photograph was taken after the accident and after the materials resulting from the explosion had been cleared away. The glass trays and 300 ml. flasks are the same as those used in the experiment. The glassware on the shelf under the hood was placed there after the accident.

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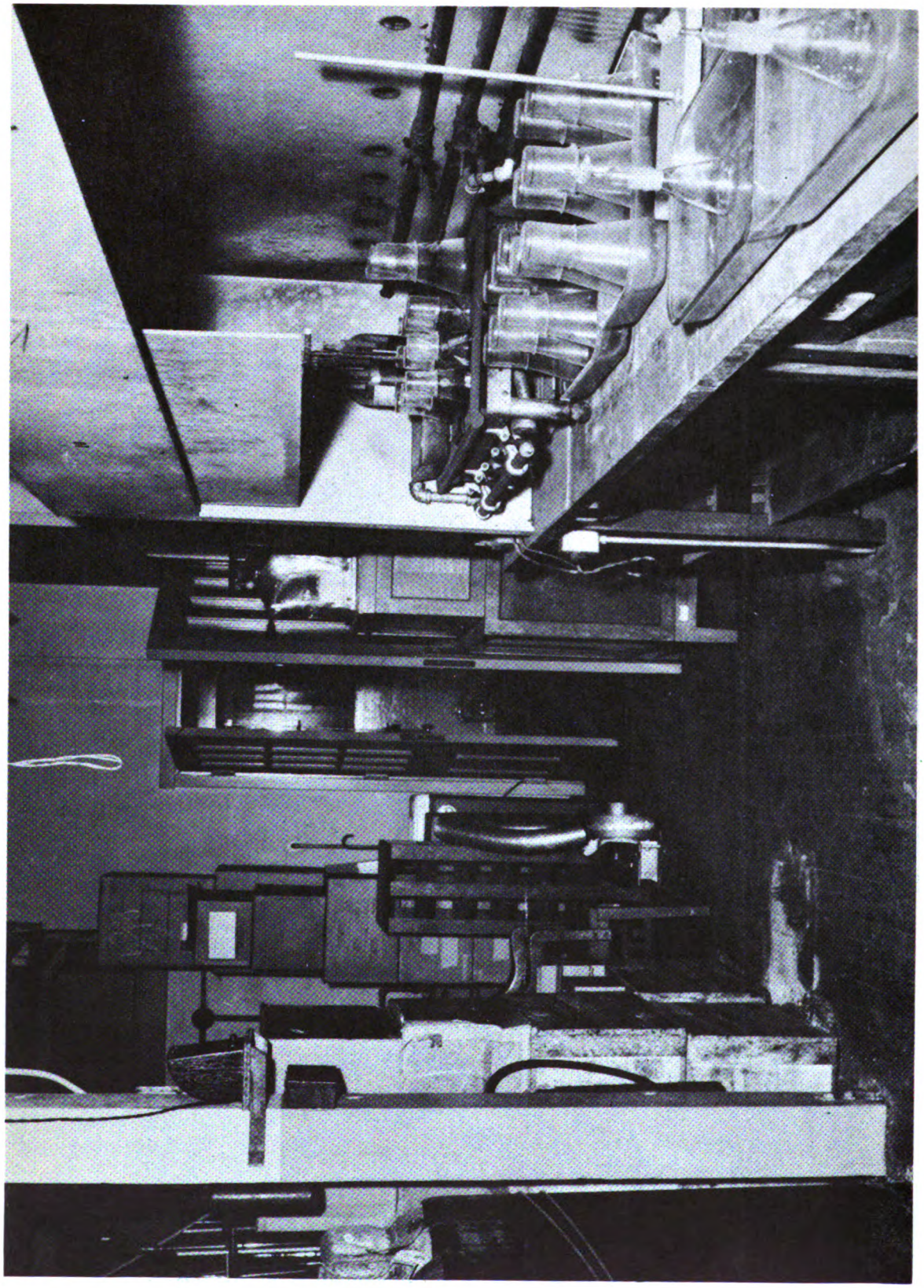

Figure 4. - A general view of the hood and surrounding area in the chemical corrosion laboratory, which shows how the acid was thrown approximately 10 feet to some storage boxes, which are well marked by acid burns.

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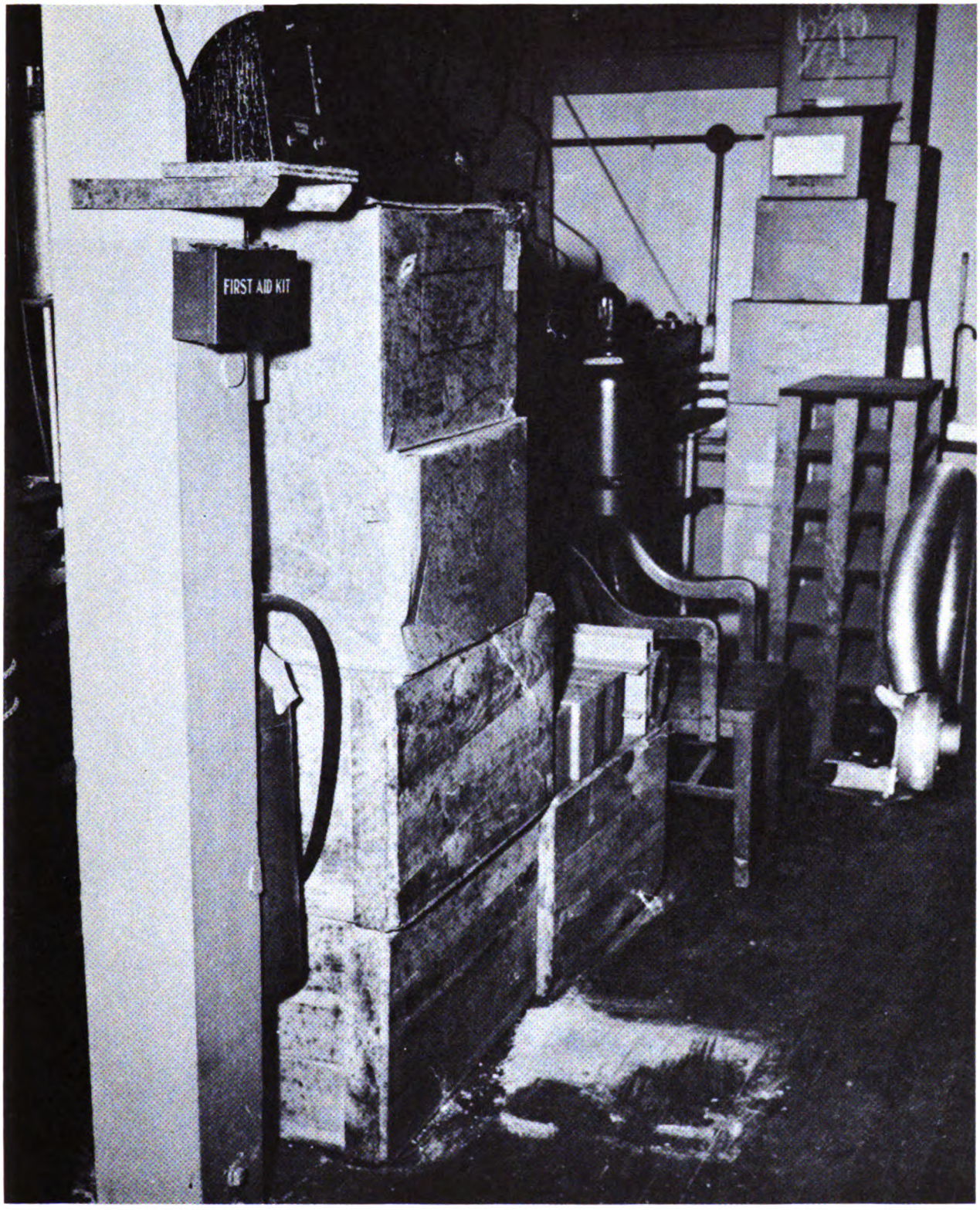

Figure 5. - A view showing acid burns on boxes approximately 10 feet from the actual explosion, which occurred on December 29.

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Figure 6. - DeVivo is used as a stand-in to show the location and position in which Acherman was found by Warfield and Green. This sink is approximately 18 feet from the hood where the explosion occurred. This hood is shown at the extreme left of the photograph.

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Figure 7. - A closeup of the sink at which Acherman was first found. DeVivo has taken the same position as witnesses remember Acherman. Note that the water is running at this sink. The witnesses believe that water was running at this sink.

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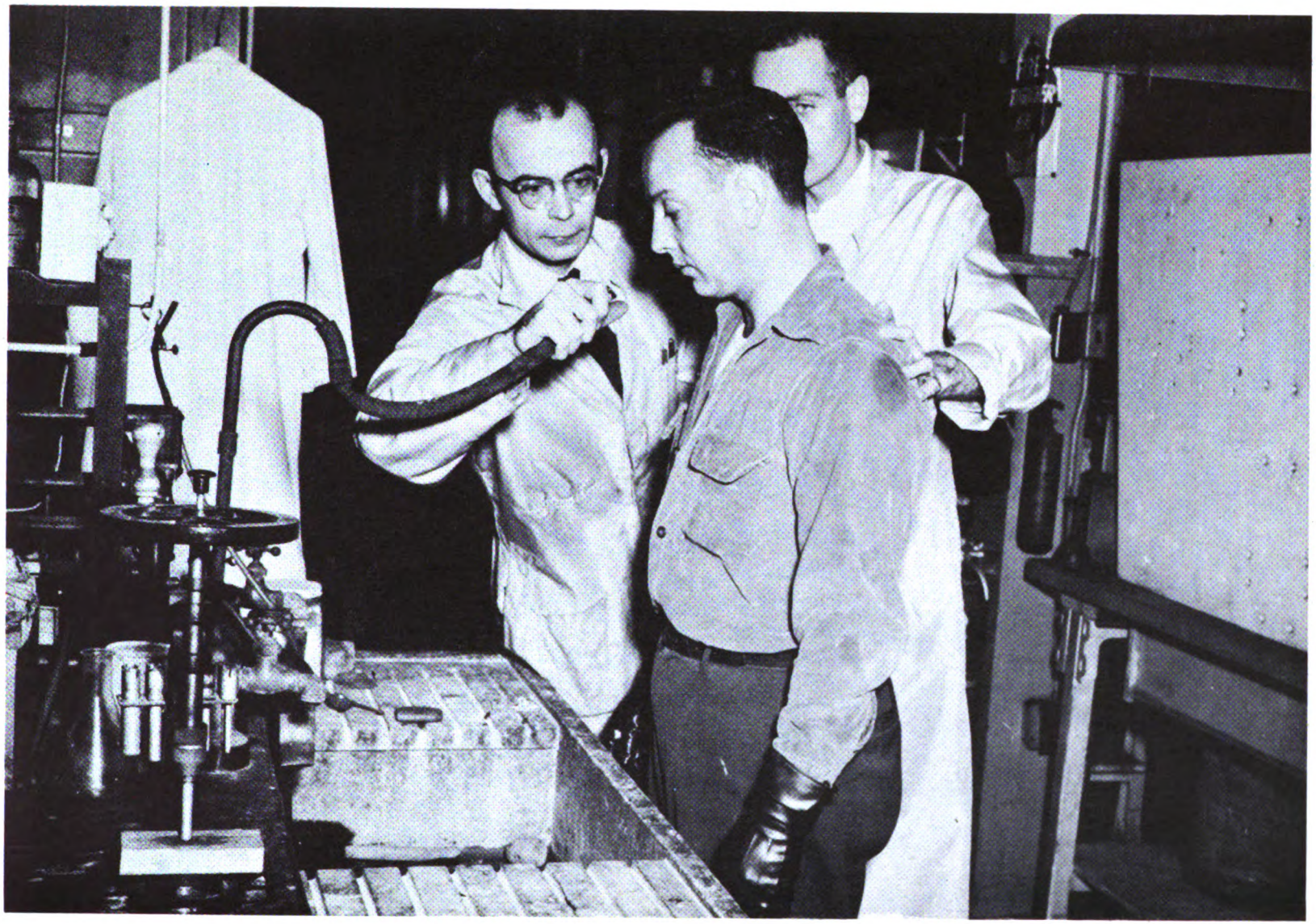

Figure 8. - Shows the sink at which the acid was washed from Acherman. The washing hose is being held by Green. The simulated victim is again DeVivo who is being supported by Warfield. This sink is approximately 14 feet from the one where Acherman was initially found. As nearly as possible, DeVivo's clothes are arranged as the witnesses remember Acherman's clothes.

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0.04 percent carbon, 0.10 percent iron, and small amounts of various other impurities. Some specimens were annealed before immersion, others were used in the cold-rolled condition. All specimens were uniformly surfaced. Corrosion rates obtained in these tests varied from 0.02 to 0.26 mil per year (m.p.y.), and the titanium specimens showed no visible signs of attack except an occasional slight discoloration. Between 1948 and 1951 there were also many experiments in which specimens of zirconium alloys (121 different alloys) were exposed to RFNA. Few, if any tests, were done with titanium in RFNA during 1951 and 1952.

Work with titanium in RFNA was resumed early in 1953, and circumstances indicate that at least some of the acid used during this period contained 20 percent dissolved NO_2. The program included stress-corrosion tests of zirconium, titanium, and titanium alloys and evaluation of titanium arc welds and spot welds. Four groups of 30-day tests designed to evaluate spot-welded titanium in RFNA were completed before December 1953. All of these tests were carried out at room temperature in vessels containing single specimens of titanium and about 250 ml. of nonaerated, quiescent acid. Specimens were cut from commercially pure, 20-percent, cold-rolled titanium sheet made from sponge by arc melting. Some specimens were annealed after spotwelding. Specimens were degreased but not surfaced before immersion in the acid. Specimens in groups 1, 2, and 4 were of a brand of unalloyed titanium (yield strength 75,000 p.s.i.) containing 0.15 percent iron and 0.06 percent carbon. Group 3 included specimens of titanium (yield strength 55,000 p.s.i.) from another manufacturer; this contained 0.21 percent iron and 0.04 percent carbon. The first three groups of experiments were done in loosely covered vessels, but the last group was carried out in tightly sealed bottles. In the first group of tests (10 specimens) the average corrosion rate was 2 m.p.y., there was stress-corrosion cracking around the perimeters of the spot welds and large losses in shear strength. In the next group of tests (20 specimens) the average corrosion rates were only 0.03 m.p.y. for annealed specimens and 0.13 m.p.y. for unannealed specimens; there was no loss of shear strength and no sign of cracking. The average corrosion rates for the third group of tests (20 specimens of low-yield-strength material) were 0.03 m.p.y. for annealed specimens and 0.72 for unannealed specimens. Again there was no loss of shear strength and no cracking. In the fourth group of tests (10 specimens) the average corrosion rate was 6 m.p.y. There was stress corrosion cracking around the perimeters of the spot welds and severe intergranualr corrosion and general embrittlement throughout the specimen. Shear strength could not be determined because the specimens usually broke at points away from the spot welds.

Tests Involved in Accident (December 22 to 29, 1953)

These tests were planned to determine the effects of such factors as cold rolling, annealing, and composition on the resistance of spot-welded titanium specimens to RFNA. The criteria were to be changes in weight, the occurrence of stress corrosion cracking around the perimeter of the spot weld, changes in shear strength of the spot weld, and general embrittlement. The spot-welded specimens used in these tests were prepared from commercially pure titantium (55,000 p.s.i. yield strength) from manufacturer A. The parent metal contained 0.4 percent iron, 0.2, carbon, 0.02, manganese, 0.02, nitrogen, and 0.005, magnesium. The sheet stock was approximately 0.040 inch thick, and each specimen consisted of two 2- by 5/8-inch pieces of metal spot welded together with 5/8-inch overlap. There were 11 groups of spot-welded specimens of 10 specimens each. Each group was treated according to one of the following procedures: Cold rolled 10, 20, 30, 40 or 50 percent[6] and spot welded; cold rolled 10, 20, 30, 40 or 50 percent spot welded, and annealed; hot

6/ Refers to reduction in thickness by cold rolling.

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rolled 50 percent at 1,200° F. and spot welded. To make it possible to correlate the results of these experiments with earlier data, 8 unwelded specimens of (75,000 p.s.i. yield strength) material from manufacturer B were included. This material contained 0.05 percent carbon, and 0.1 percent iron, and the same percentages of the other elements mentioned above. Half of these specimens were cold rolled, and the other half were cold rolled and annealed in vacuum at 800° C. All specimens of both types had sheared edges, and some also had rolled edges. The specimens were degreased and weighed before being immersed in acid. Spot-welded specimens were immersed in 300-ml. Erlenmeyer flasks equipped with stoppers with ground glass joints and stopcocks. The stopcocks were lubricated with a silicone stopcock grease; the ground-glass flask joints were not lubricated. Five specimens were placed in each flask with about 290 ml. of RFNA, enough to cover all specimens with at least one-fourth inch of solution. This left approximately 50 ml. of void space in each flask and joint. The position of the specimens in the flasks may be described as approximately vertical or at small angles from the vertical. The single specimens were placed in similar 250-ml. flasks, 4 specimens per vessel.

Tests with 108 spot-welded and single titanium specimens were begun between 1 and 4 p.m. on December 22. The remaining 10 specimens, spot-welded, hot-rolled titanium sheet, were immersed in 2 flasks at 1:45 p.m. on December 28. The 22 flasks, containing 108 specimens, were vented daily for 6 days before December 29. The remaining two flasks started on December 28, were not vented before December 29.

Evidently the corrosion processes, which took place between December 22 and 29, yielded pyrophoric material (probably finely divided titanium) on certain titanium specimens. Some of this material was disturbed by Acherman as he vented the flasks, and a rapid reaction with RFNA followed. A large amount of heat was liberated, resulting in oxidation and even fusion of metal. Perhaps the shock displaced pyrophoric material on other specimens, causing more reaction and liberation of more heat.

Members of the Physical Metallurgy Branch at College Park made an exhaustive study of the titanium specimens involved in the accident (complete metallurgical report in appendix). The specimens of low-yield-strength material showed much higher weight losses than titanium had ever shown before in this corrodant. Specimens were attacked in various ways and at several points, depending on their preimmersion history, but all specimens were attacked. There was much evidence of the formation and spattering of molten metal, especially at sheared edges. Specimens of the high-yield-strength material did not undergo large weight losses but did show signs of extensive intergranular corrosion.

Reports on Tests in Other Laboratories

During the second half of 1953 notes appeared in Metal Progress and in several suppliers' publications to the effect that violent reactions had occurred in several instances when a titanium-manganese alloy had been immersed in RFNA. One of these incidents is known to have occurred in the laboratories of the North American Aviation Co. at Downey, Calif., when several test specimens of a titanium - 8-percent - manganese alloy reacted with RFNA, showering a chemist with corrosive liquid. The specimens were attacked and pitted, and there was evidence of fused material. Commercially pure titanium in the same test was unattacked, giving rise to the theory that the presence of manganese was necessary for reaction and that no trouble would ensue from the combination of commercially pure titanium and RFNA.

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BEHAVIOR OF TITANIUM IN RED-FUMING NITRIC ACID

Data on the behavior of commercially pure titanium in RFNA, summarized above and in the appendix, are inconsistent. Titanium was almost inert in tests carried out from 1948 to 1950 but was attacked by this acid in many instances during 1953. Such attack was evidenced in one or more of the following ways: Changes in weight, cracking at the spot weld, intergranular corrosion and general embrittlement, and formation of pyrophoric material followed by violent chemical reaction. The only occasion when pyrophoric material is known to have formed and reacted on commercially pure titanium was at College Park on December 29. There is no completely satisfactory explanation for this solitary occurrence. However, a review of all available information suggests that certain conditions may have had an important part in the pbenomenon. These ideas are presented below in the hope that they may serve as a basis for safety measures or for planning future experiments in this field.

The presence of relatively large amounts of iron and carbon as impurities in titanium may be important in the formation of pyrophoric material. Those specimens heavily involved in the violent reaction of December 29, as shown by large weight losses and the presence of oxidized or fused metal, contained unusually high percentages of iron and carbon. On the other hand, specimens that were relatively low in iron and carbon never exhibited a tendency to react violently, although they have undergone sizable weight losses and have shown signs of intergranular corrosion and general embrittlement. Moreover, the manganese content of all specimens concerned is low, indicating that the presence of manganese is not necessary for forming pyrophoric material and subsequent reactions.

Stresses seem to increase the tendency for titanium to corrode in RFNA but may or may not be important in forming pyrophoric material. Special stress-corrosion tests indicated that titanium and some of its alloys are susceptible to cracking in RFNA, but there was no evidence of unusual reactivity. Fused and oxidized material seemed to be concentrated at the sheared edges of those specimens from the tests of December 22-29 that were cold rolled and not stress relieved. On the other hand, fused metal was also detected in pits on the flat surfaces of specimens that were annealed. The hot-rolled specimens had the highest corrosion rate, and this corrosion was largely at the sheared edges. Cracking in the spot-weld area was common, but there was virtually no evidence of molten metal.

The composition of the RFNA may be important. Titanium was resistant in early tests with acid containing 92 percent nitric acid, 6.5 percent nitrogen dioxide, and 1.5 percent water. However, this work is not comparable to the work of 1953 because the tests at that time were all made in loosely covered vessels with titanium specimens that were very low in iron and carbon and had milled edges and abraded surfaces. The behavior of titanium varied greatly in tests during 1953. The acid used in at least some of these tests contained 20 percent nitrogen dioxide.

Certain features of the experimental method may also be important. In this laboratory, sealed vessels were used with RFNA in only two groups of tests. On the first occasion, 10 specimens of 75,000 p.s.i. yield-strength material underwent very severe intergranular corrosion and embrittlement. The accident of December 29 occurred the second time sealed bottles were used. The omission of surfacing in preparing specimens and the use of hot-rolled sheet may be significant because it resulted in large, inactive, oxidized surfaces in contact with small, active, sheared edges. Finally, immersion of 5 specimens in each of 22 flasks with relatively small volumes of corrodant and frequent contact between specimens may have some bearing on what happened.

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CAUSES OF THE ACCIDENT

The causes of the accident have not been determined. The conclusions reached are:

1. Mechanical movement of the equipment probably initiated the chain of events that resulted in the accident under investigation.

2. The greatest concentration of corrosion at the sheared edges of the specimens examined occurred when the metal was hot rolled and sheared. This may have been caused by electrochemical effects between the active sheared edges and the relatively inert oxidized surfaces.

3. Two grades of titanium were involved in the test; both suffered corrosion. The grade containing the higher percentages of iron and carbon showed the greater corrosion. The function of either or both of these elements in producing an unsafe condition in RFNA is uncertain; however, the loss of iron in badly corroded areas indicates that the high iron may be a factor worth considering.

4. Metallographic studies show intergranular corrosion in all stress-corroded areas in unannealed samples and in the pitted surface areas of annealed samples. Intergranular corrosion might cause the generation of powdered metal, which is pyrophoric. Deep fissuring and loss of molten material at sheared edges indicate that this type of stress corrosion was a major source of phyrophoric material.

5. Metallographic studies showed oxidation and in some instances fusion of corroded material. This indicates that considerable heat was generated, which might have been caused by a rapid reaction between pyrophoric material produced by corrosion processes and RFNA.

6. There is no clean evidence that the spot welds of themselves had any part in bringing about the explosion.

7. The possibility of formation of an explosive decomposition product of RFNA, such as hydrazoic acid, in this reaction should not be ignored. Proof of the existence of such a product, however, is not at present possible.

RECOMMENDATIONS

The following recommendations are made regarding the cause of the accident:

1. The mechanism of this particular occurrence should be determined more positively and others interested in the uses of titanium should be informed of the results. A research program is now in progress in cooperation with industry to determine the characteristics of the metal and its alloys in RFNA. Depending on the results of such research, the program might well be expanded or continued to include other reactions.

2. Until this information becomes available, it is recommended that any contact of titanium or its alloys with RFNA or other strong oxidizing liquids be considered potentially dangerous from the explosion standpoint and that proper precautions be taken at all times.

Recommendations for protection of personnel conducting the investigation are:

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1. That written operating instruction shall be prepared to include specific safety precautions for any corrosion tests with potentially dangerous materials and shall include the following:

a. All of the operations shall be performed in an acid hood with the vacuum system in operation or in an isolated area where the specimens and acid may handled by remote control.

b. At least minimum personal protection shall be used, including face shield or goggles and working behind protective barrier, laboratory apron or laboratory coat, and polyethylene gloves (rubber or neoprene gloves are not recommended for RFNA).

2. Properly working protective respiratory devices shall be available at all times, and the men shall be trained in the use of these devices. An All Service gas mask with All Service canister is preferable.

3. Properly functioning emergency showers shall be available at all times.

APPENDIX

METALLURGICAL INVESTIGATION INTO THE CAUSE OF AN EXPLOSION INVOLVING SPOT-WELDED TITANIUM SPECIMENS IN RED FUMING NITRIC ACID

Introduction

On December 29, 1953, an explosion occurred while stress-corrosion tests were being conducted on spot-welded titanium samples in red fuming nitric acid, hereinafter referred to as RFNA. The explosion was violent enough to throw spot-welded samples weighing approximately 8 grams 20 feet. The chemist who was venting a stopcock on an acid flask at the moment of the explosion was severely burned over large areas of the body. Involved in the detonation were 24 Erlenmeyer flasks, each containing about 250 ml. of RFNA, and 5 spot-welded specimens.

Previous experiments conducted by the late L. B. Golden showed titanium to be subject to stress-corrosion cracking when exposed to RFNA. The experiment under discussion was set up to determine to what extent spot welds on titanium strip stressed to various degrees would be attacked.

Specimens Involved

The following series of samples figured in the test under way when the explosion occurred:

(a) Unalloyed titanium (yield strength 55,000 p.s.i.) from manufacturer A, cold rolled 10, 20, 30, 40, and 50 percent, and spot welded. Ten samples for each percentage of cold roll (that is, 50 samples in all).

(b) Same as (a) except all samples were vacuum annealed at 800° C. after spot welding.

(c) Same material as in (a) and (b), warm rolled 50 percent at 1,200° F. and spot welded. Ten samples.

(d) Unalloyed titanium (yield strength, 75,000 p.s.i.) from manufacturer B, as cold rolled. Four samples.

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(e) Same as (d), except samples were vacuum annealed at 800° C.

Sample series (a) represents stress by various degrees of cold rolling, whereas sample series (c) was stressed by warm rolling. The stresses set up on the edge of the sample by shearing were not considered at the time. Aside from these objectives, control samples were prepared to run more or less concurrently. Series (b) samples were run to check the influence of post annealing on spot weld attack. Series (d) and (e) samples represent titanium strip obtained from a different source, and hence of different compositon, in the cold-rolled and annealed condition, respectively.

The conditions of the experiment were to submerge the samples in RFNA for 30 days at room temperature under static, nonaerated conditions at atmospheric pressure or slightly above. Twenty-four Erlenmeyer flasks (250 cc.) were used, each flask containing 5 titanium samples. The flasks had ground glass joints with stopcocks to keep the samples nonaerated and to make it possible to relieve pressure buildup by venting the flasks daily. No pressure buildup was noted at the moment of the explosion, at which instant the chemist in charge had finished venting a flask.

The spot-welded samples of 0.041-inch thick stock, were approximately 5/8 inch wide by 3-1/2 inches long. Series (d) and (e) samples, also 0.041 inch thick, were cut 5/8 inch wide by 2 inches long. All samples, except those of series (c), ran 7.11 days; those of series (c) received only 1 day exposure before the explosion.

Since the explosion shattered the flasks and scattered the samples, the only means of identification was scribe markings on the individual samples, which in many instances were corroded away. Of the 118 samples under test, 99 were identified, 15 were corroded beyond identification, and 4 were lost. All the unidentified samples were of series (b); this group had received a high degree of surface pitting.

Corrosion Test Results

Preliminary examination of the samples revealed several types of corrosion, some of which were unique to this experiment. It was therefore considered advisable to determine not only the corrosion rate for each sample based on loss in weight but also to establish definitive standards (types) of corrosive attack and to catalog each sample as to the severity of each corrosion form. Accordingly, photomacrographs were made of representative corrosion forms. These are presented in figures 9-15 for further reference. Four general types of attack were observed, namely:

1. Staining (dark gray to blue).
2. Pitting.
3. General attack.
4. Stress-corrosion cracking:
   - (a) At spot-weld indentation.
   - (b) At rolled edges (some samples possessed edges from the original as-rolled sheet).
   - (c) At sheared edges.

Staining attack (note figure 9A) was confined to the series (d) samples. Figure 9B, is a spot-welded titanium strip from manufacturer B exposed to RFNA for 30 days in a previous experiment in November 1953. The same staining is observed here in a more pronounced stage, owing to the longer exposure time.

Pitting attack was observed in the (a), (b), and (e) sample series. It was accompanied by dark-gray staining around the pit edges (note fig. 10, arrow X),

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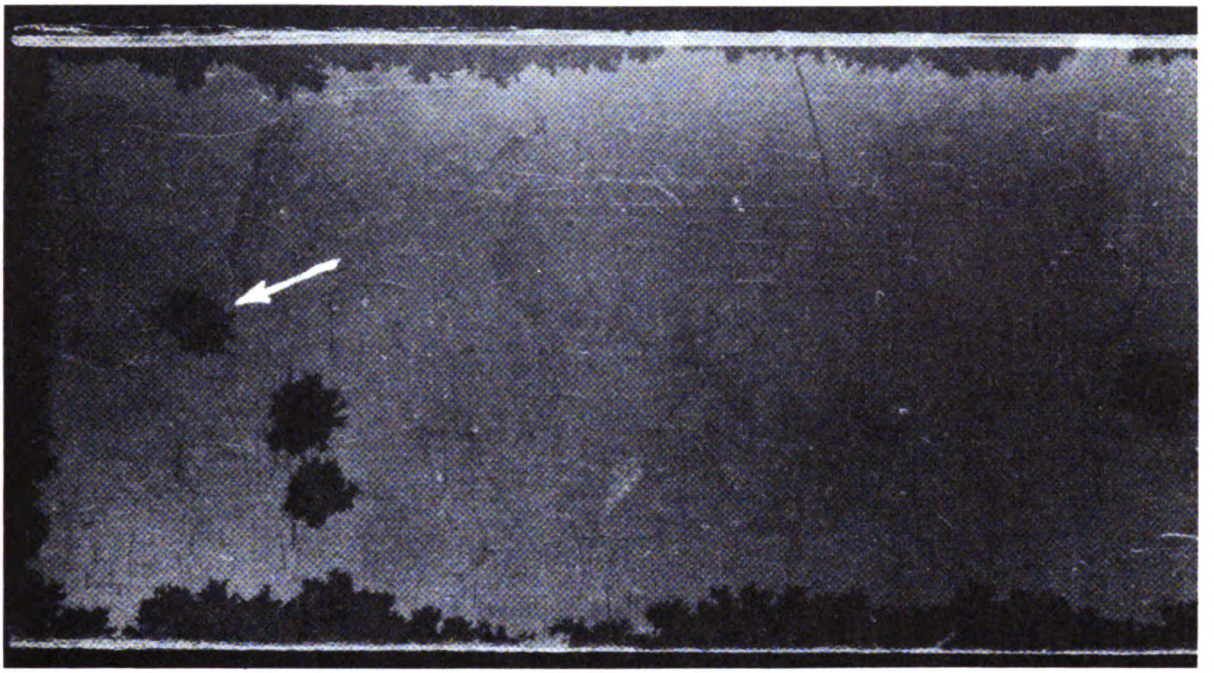

5X

Figure 9A. - Surface staining attack in a cold-rolled, series (d) sample.

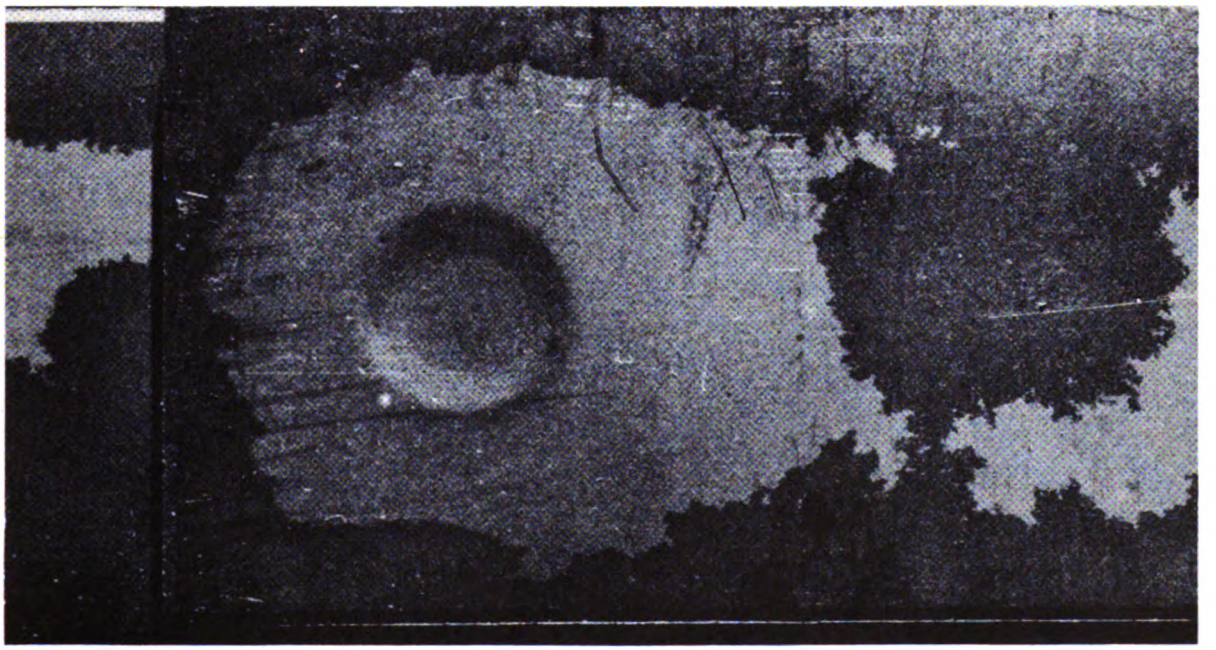

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Figure 9B. - Staining attack in cold-rolled, spot-welded titanium from the same heat as figure 9A exposed to RFNA for 30 days in an earlier run.

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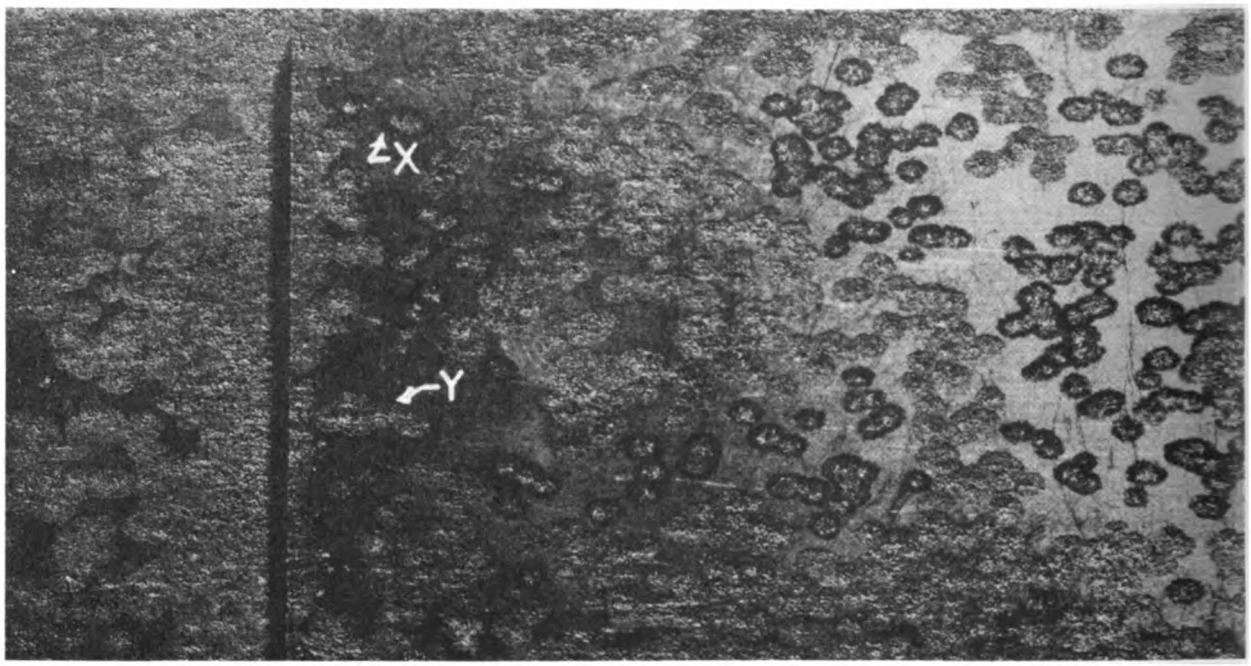

5X

Figure 10. - Surface pitting attack observed in annealed series (b) spot welds. Arrow at X indicates pits unaltered by the explosion. Pits at Y were oxidized during the explosion.

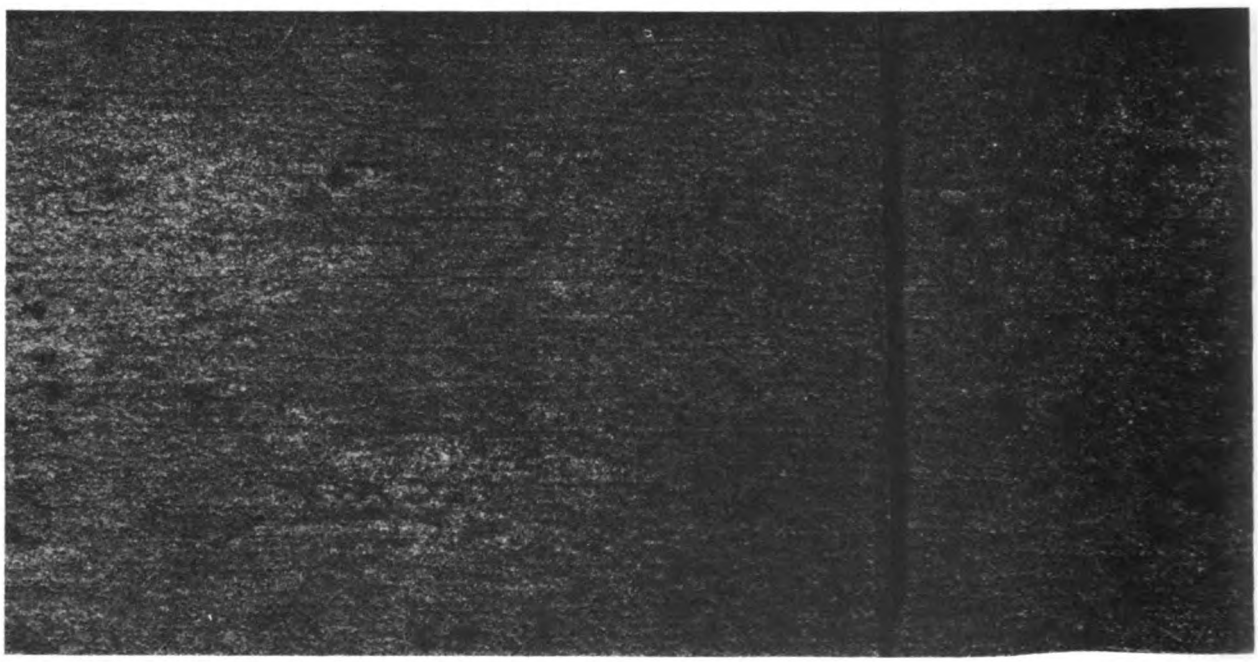

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Figure 11. - General attack in series (b) spot-weld samples. This is an advanced form of the pitting attack observed in figure 10.

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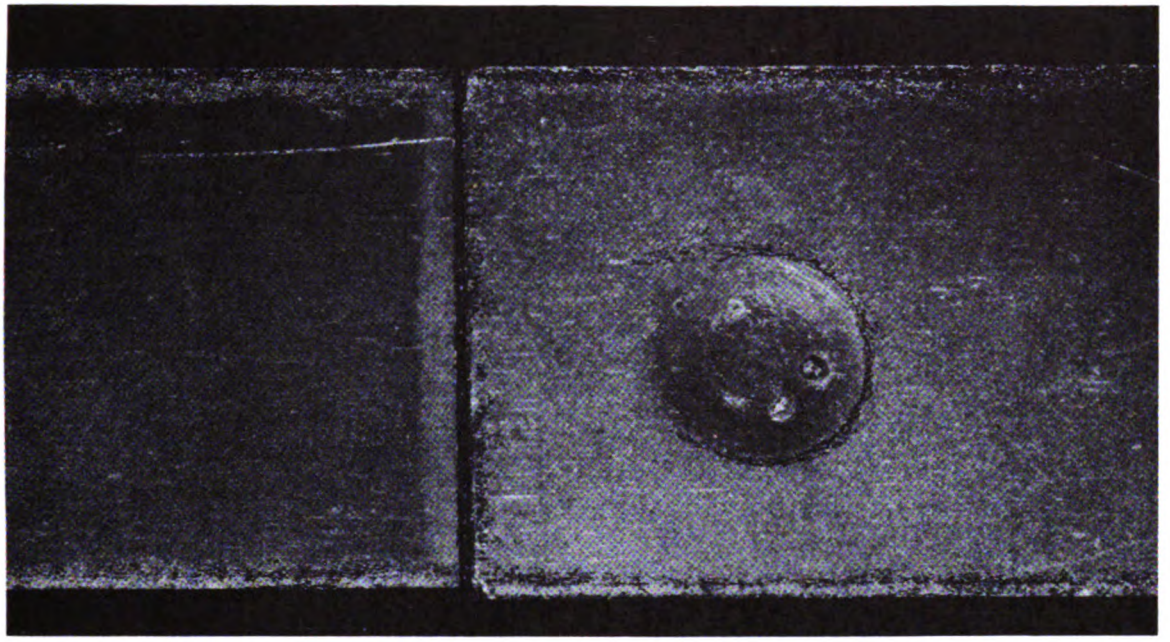

5X

Figure 12. - Stress-corrosion cracking along periphery of spot-weld indentation observed in unannealed, series (a) and (c) samples.

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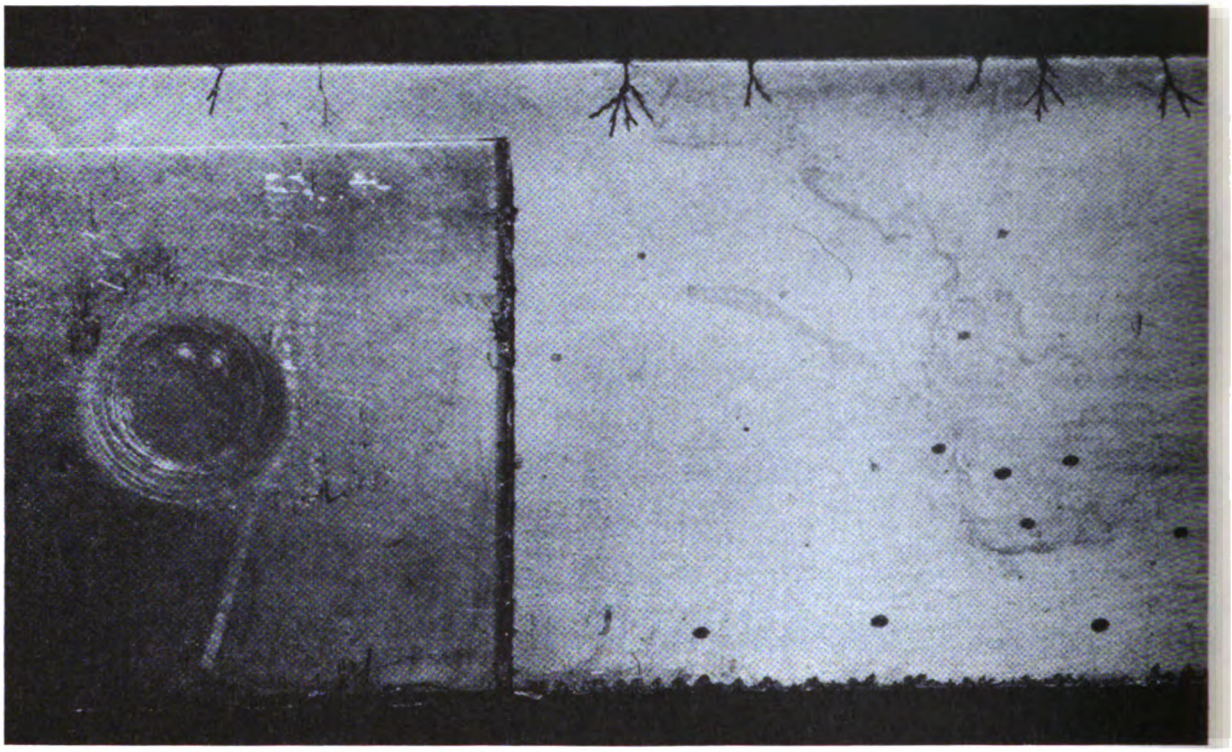
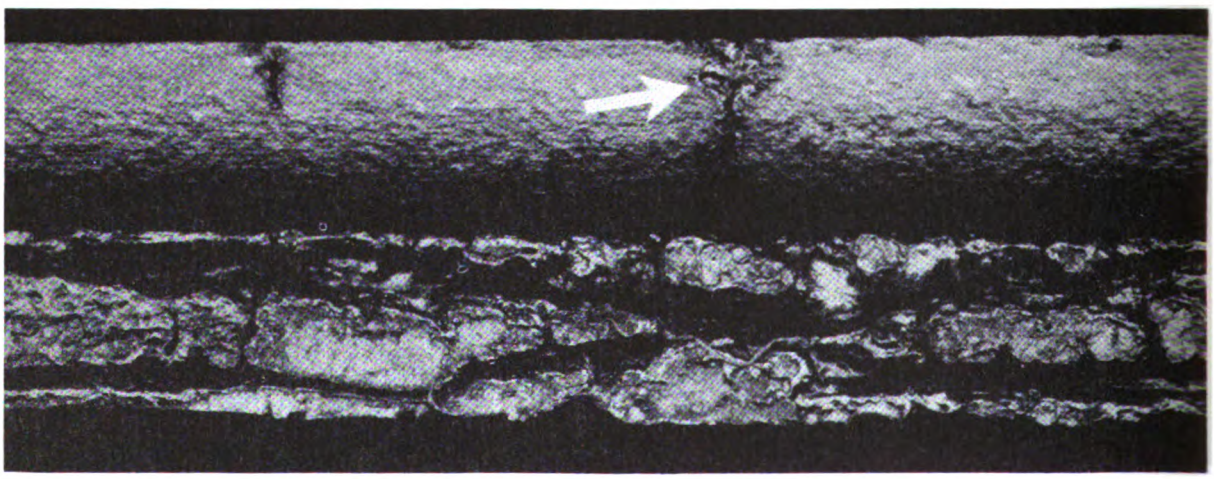


5X

Figure 13. - Stress corrosion cracking propagating in a tree-like pattern from rolled edge at top. Bottom edge is sheared.



25X

Figure 14. - Edge view of stress corrosion at rolled edge (top sample). Arrow indicates expulsion of molten material. The rolled edge sample was spot welded to a sheared edge sample seen in lower half of field.

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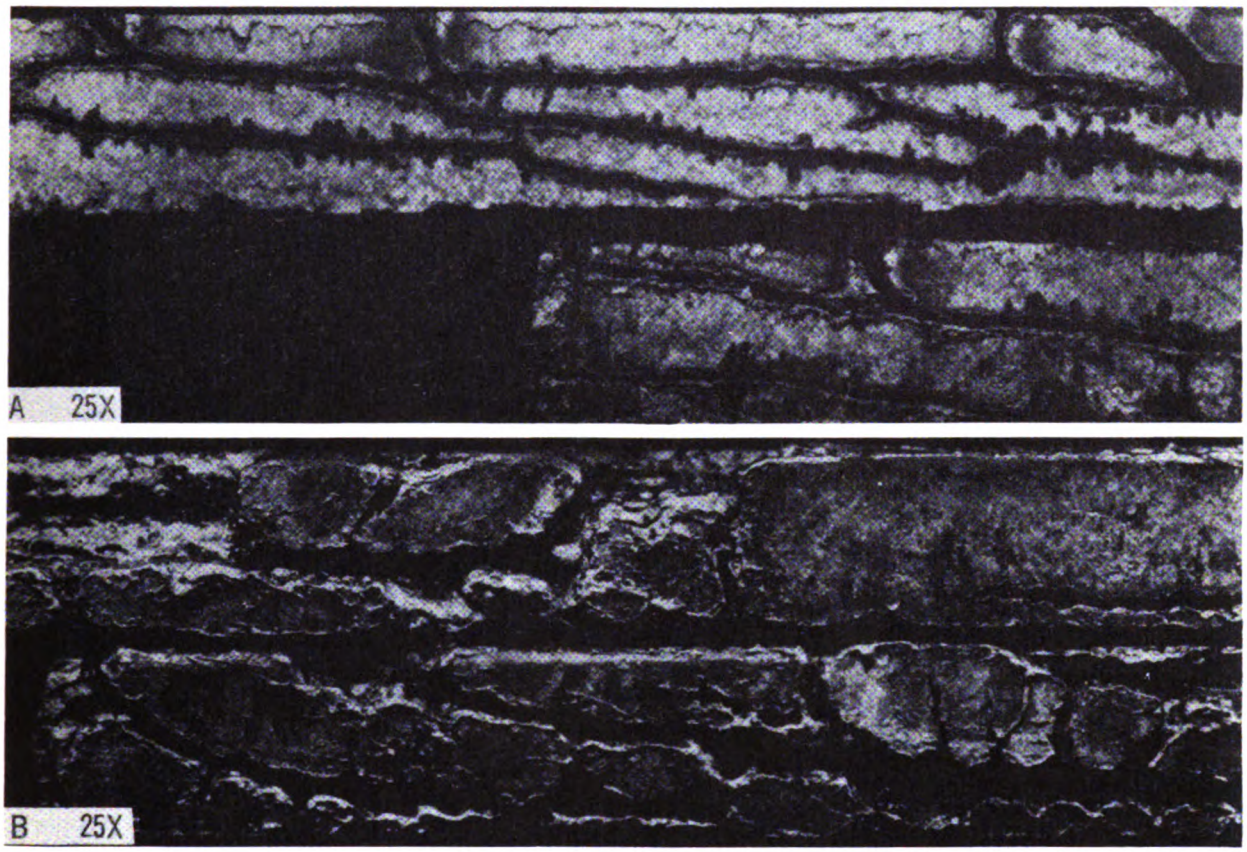

Figure 15A. - Edge view of spot welded samples with different degrees of sheared edge attack; figure 15B shows a more advanced attack.

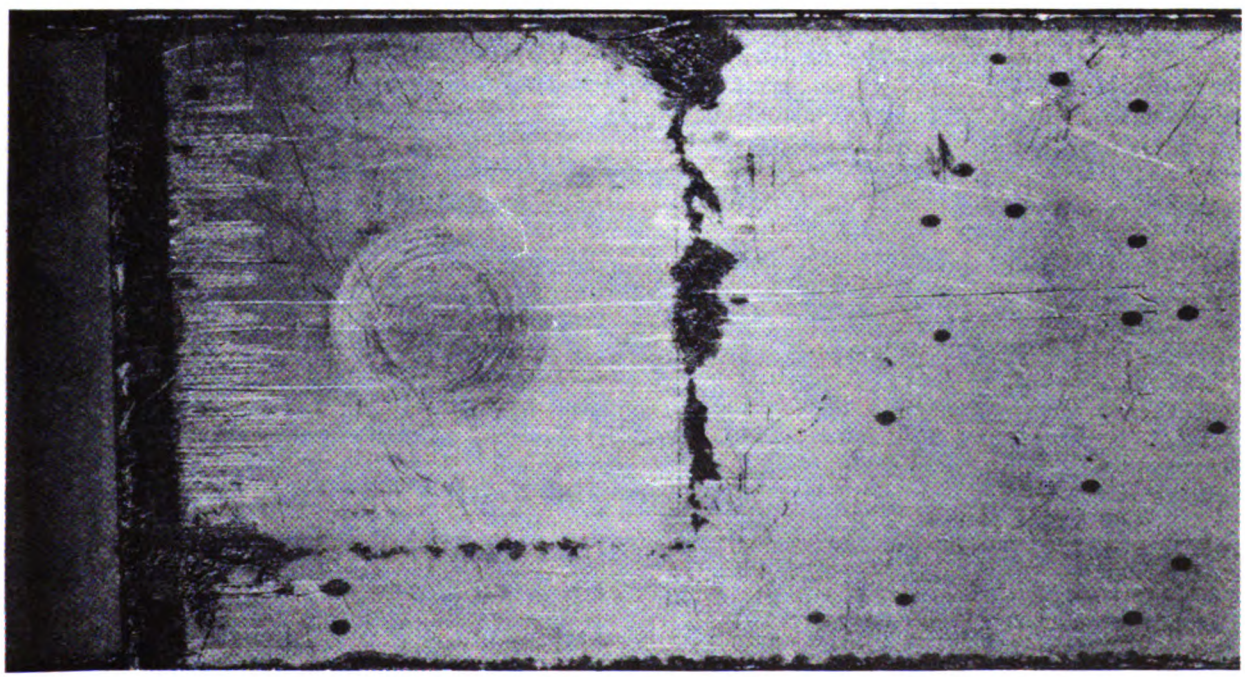

Figure 16. - Spatter from sheared edge of overlying sample outlining the region of overlap. 5X

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except in those pits where ignition occurred during the course of the explosion resulting in oxidation (burning). The latter pits showed oxidation of both the pitted and stained area. The oxidation products are identified by a prismatic array of color, which photographed gray (note fig. 10, arrow Y).

General attack is illustrated in figure 11; it appeared only in the annealed samples (that is, series (b) and (e)). This attack is actually an advanced form of pitting where the entire area has become pitted and the metal has been etched deeply enough to reveal the rolling texture.

Three forms of stress-corrosion cracking are seen in figures 12-15. In spot welds the stress corrosion cracking followed the periphery of the indentation (note fig. 12). Two views of stress cracking at a rolled edge are observed in figures 13 and 14. The stress corrosion is observed in figure 13 to propagate in a tree pattern from the rolled edges. Stress attack at sheared edges is illustrated in figures 15 A and B. Here edge views of samples with different degrees of attack are shown.

At the sheared edges corrosion was deep, and oxidation of disintegrated material generated enough heat to cause melting and spatter. These features are seen in figures 15A and B. Since the samples were overlapping in the nitric-acid solution, expulsion of molten material from corrosion fissures along the sheared edges was found in several cases to have spattered on the underlying sample, thus outlining the region of overlap (note fig. 16). In figure 14 some expulsion of molten material is noted from a transverse crack at a rolled edge. Only minor amounts of spatter were observed emanating from the cracks at spot indentations.

A detailed study was made of all samples recovered from the explosion to determine to what extent each sample series (a), (b), (c), (d), and (e) underwent the various forms of corrosive attack discussed under corrosion types. Of equal concern was the degree of oxidation of the corroded products, since this information would indicate the test group or test procedure contributing most to the severity of the explosion. Test results are tabulated in table 1.

The highest corrosion rate (115.5 m.p.y.) is observed in the warm-rolled, spot-weld group, series (c), and occurred almost exclusively at the sheared edges. Since this series ran only 1 day, the results cannot be used for comparison purposes; nevertheless, it is significant to note that the gullying and fusion at the sheared edges were almost as severe in these samples as they were in those of series (a), exposed 7.11 days.

Edge attack likewise accounted for a major portion of the attack in the series (a) sample group. It is observed that the 20- and 30-percent cold-roll samples had the highest attack in all of the corrosion forms tabulated, with a falling off at greater and lower percentages of cold work.

Corrosion weight loss in the annealed spot welds, series (b), is credited largely to extensive surface pitting attack - several times greater than for the corresponding cold-rolled samples. No localized attack at the sheared edges or spot-weld area was observed in either of the annealed series (b) or (e), indicating total absence of stress-corrosion attack.

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TABLE 1. - Test results, sample series

	From manufacturer A										From manufacturer B		
	(a) Cold-rolled, percent					(b) Cold-rolled and annealed, percent					(c) Hot-rolled	(d) As rolled	(e) Annealed
	10	20	30	40	50	10	20	30	40	50			
Corrosion rate.....m.p.y.	27.4	59.7	42.1	17.9	17.9	35.2	54.4	61.6	55.4	66.9	115.5	1.1	3.0
Exposure time.....	7.11 days					7.11 days					1.0 days	7.11 days	7.11 days
Spot-weld area:													
Description of attack.....	Cracking					Pitting					Cracking	-	-
Area affected.....percent	1/20	78	62	0	10	2/33	36	57	53	68	1/32		
Sheared edges:													
Description of attack.....	Gullying					Pitting					Gullying	Cracking	Pitting
Edge affected.....percent	40	100	70	25	30	33	36	57	53	68	25	5	50
Affected area oxidized....													
.....percent	100	100	100	100	100	54	55	92	50	50	100	0	0
Sample surface:													
Description of attack.....	Pitting					Pitted					Pitted	Stain	Pitted
Surface affected...percent	0.4	13	14	9	3	33	36	57	53	68	6	5	50
Affected area oxidized....													
.....percent	0	2	2	2	0	54	55	92	50	50	100	0	0

1/ Percentage of indented spot-weld periphery cracked.
2/ Percentage of spot-weld area pitted.

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The surface attack on the annealed material from manufacturer B, sample series (e), covered the same surface area (that is, 50 percent) as the average attack on the corresponding material from manufacturer A sample series (b). This similarity of attack was not found in the cold-rolled samples. Here the cold-rolled series (d) samples showed a staining type of surface attack, whereas the corresponding series (a) material exhibited a pitted type of surface attack.

Differences in composition in the two sample sources will be discussed in the paragraphs on analytical studies. Suffice it to say here that the explosion apparently did not originate in the samples of the (d) and (e) series, since no evidence of oxidation was observed here.

Metallographic Studies

Selected metallographic sections of corroded and fused areas were examined to determine the nature of corrosion propagation.

In the study of the behavior of staining attack, as illustrated in figures 9A and B, an isolated stain patch was selected for examination, note arrow in figure 9A. This area was chosen to eliminate any stress influence from the sheared edges. The metal underlying the stained area after removing 0.002 inch from the surface, showed extensive intergranular attack, note upper field of photomicrograph figure 17. The lower field in this figure underlies the adjacent unattacked surface area. A transverse section thru a stained area of the sample in figure 9B, exposed to RFNA in an earlier run for 30 days without mishap, showed the intergranular attack to penetrate halfway thru the sample thickness (0.041 inch) (note fig. 18). Although the weight loss here was moderate (6.32 m.p.y.), the metal was easily broken with the fingers and exhibited a dull ring when struck. Staining, as illustrated, was thus found to indicate subsurface intergranular attack, and its occurrence was limited to the stock from manufacturer B.

To determine the nature and depth of pitting attack, a transverse section was made through an unignited pit, similar to X in figure 10. The pit is seen in transverse section in figure 19 to be intergranularly corroded, the depth of corrosion being quite shallow (approx. 0.0006 inch depth). Ignition of pitted areas was extensive in the annealed series (b) samples and, judging from the areas affected, contributed significantly to the force of the blast.

Stress-corrosion cracking in unannealed spot welds was found to be largely confined to the outer periphery of the electrode indentation (note fig. 12). The cracking, for the most part, penetrated the thickness of the strip along a path outside the weld nugget and heat-affected zone. These features are seen in figure 20, a transverse section through the center of series (a) spot weld. It would thus appear that stress-corrosion cracking in spot welds is a function of surface stresses set up at the electrode periphery.

Although comparatively few samples in the explosion run had rolled edges (that is, they had edges of the original as-rolled sheet), it is noteworthy that attack from this stress source (see figs. 13 and 14) was quite extensive. Photomicrographs (figs. 21 and 22) made in this area after the surface was ground show the attack to be intergranular.

Sheared-edge samples of series (a) and (c), showing edge attack similar to that seen in figures 15A and B, were sectioned transversely to determine the depth and nature of this type of attack. Figures 23A and B, are photomicrographs of series (a)

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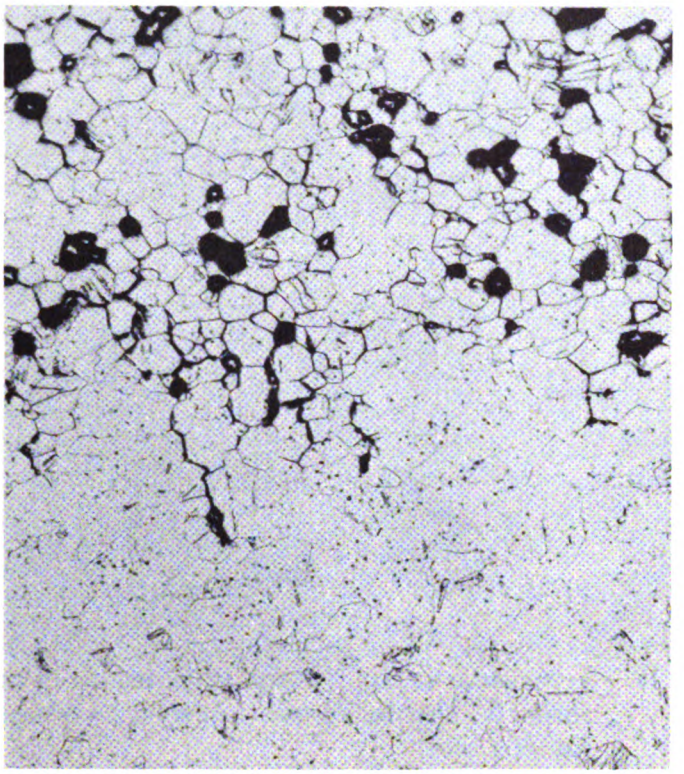
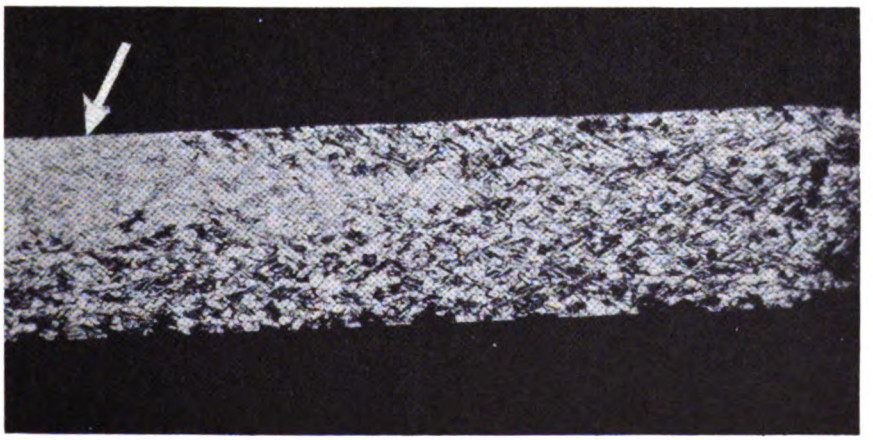


X100

Figure 17. - Micrograph of structure underlying stained area at arrow in figure 9A. Top half of field underlying stained area shows intergranular attack. Keller's etch.



25X

Figure 18. - Section through stained and unattacked surface seen in figure 9B. Arrow indicates unattacked (unstained) surface. Keller's etch.

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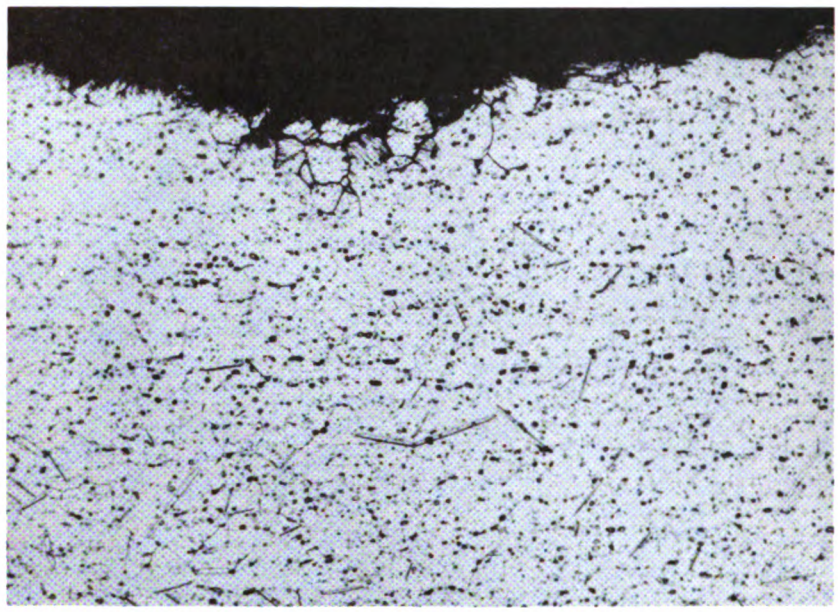
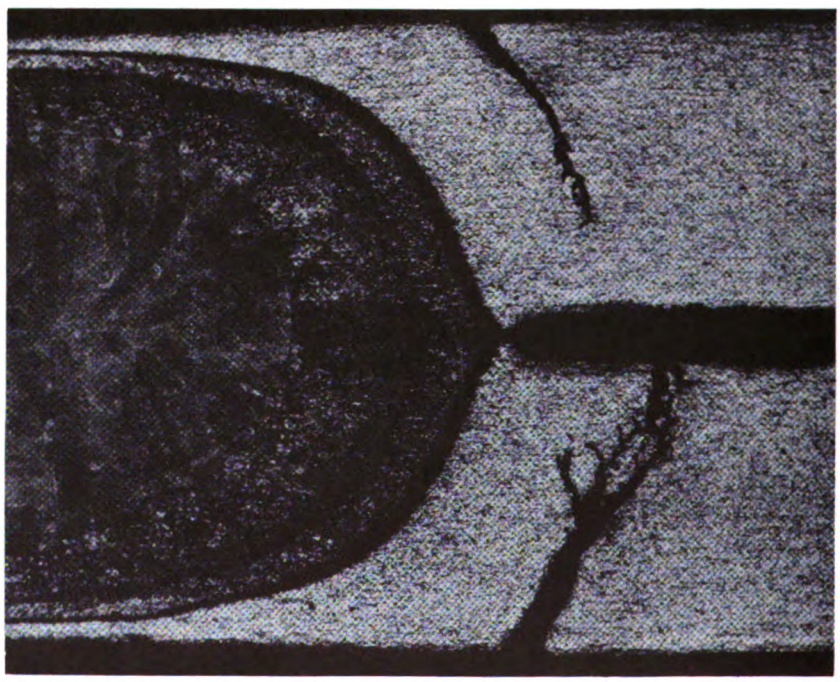


X100

Figure 19. - Transverse section through unignited pit is annealed, series (b) sample. Attack is seen to be intergranular. Keller's etch.



35X

Figure 20. - Transverse section through a series (a) spot weld. Spot-weld perimeter cracking is seen to be removed from heat-affected zone. Keller's etch.

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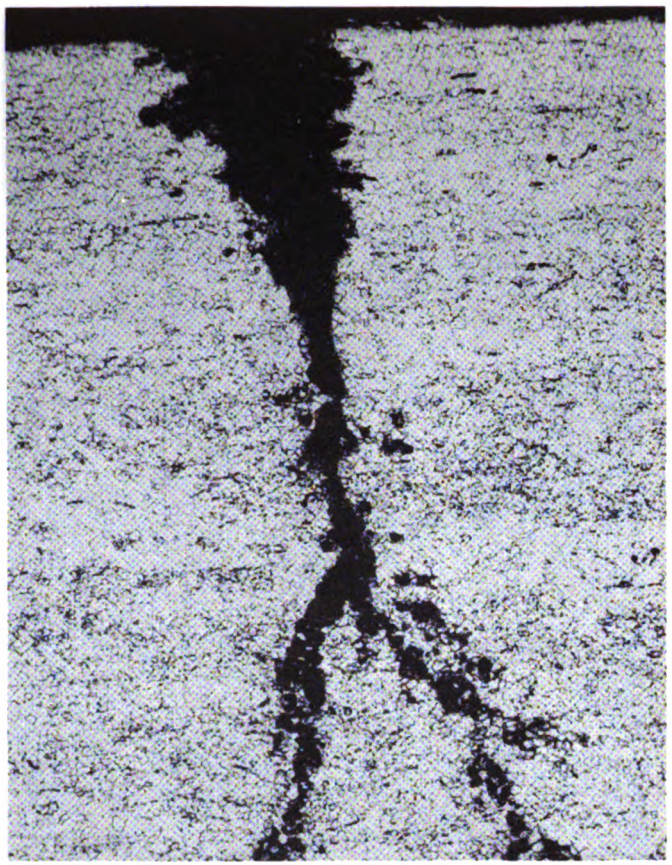
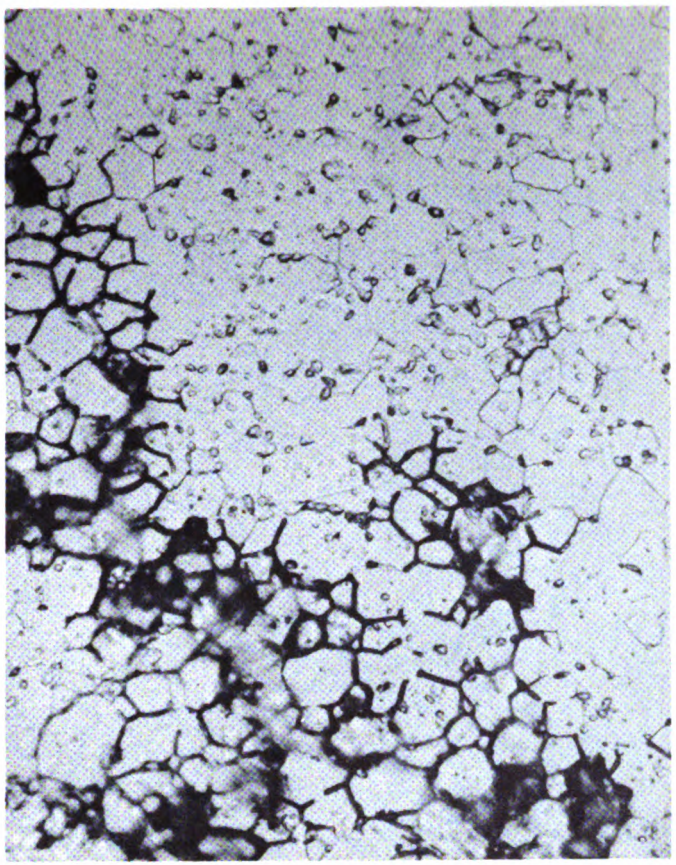


100X

Figure 21. - Micrograph of cracking at rolled edges shown in figure 13. Field shown is parallel to the surface. Keller's etch.



500X

Figure 22. - Same area as figure 21, cracking is seen to be intergranular. Keller's etch.

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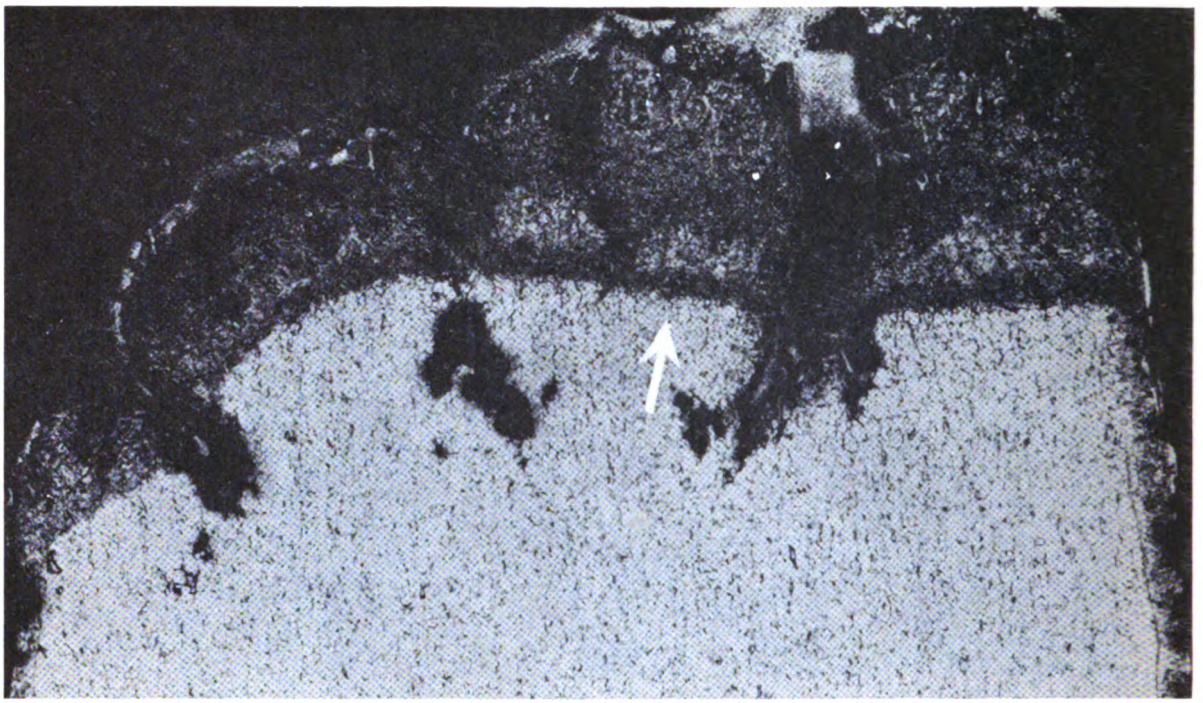
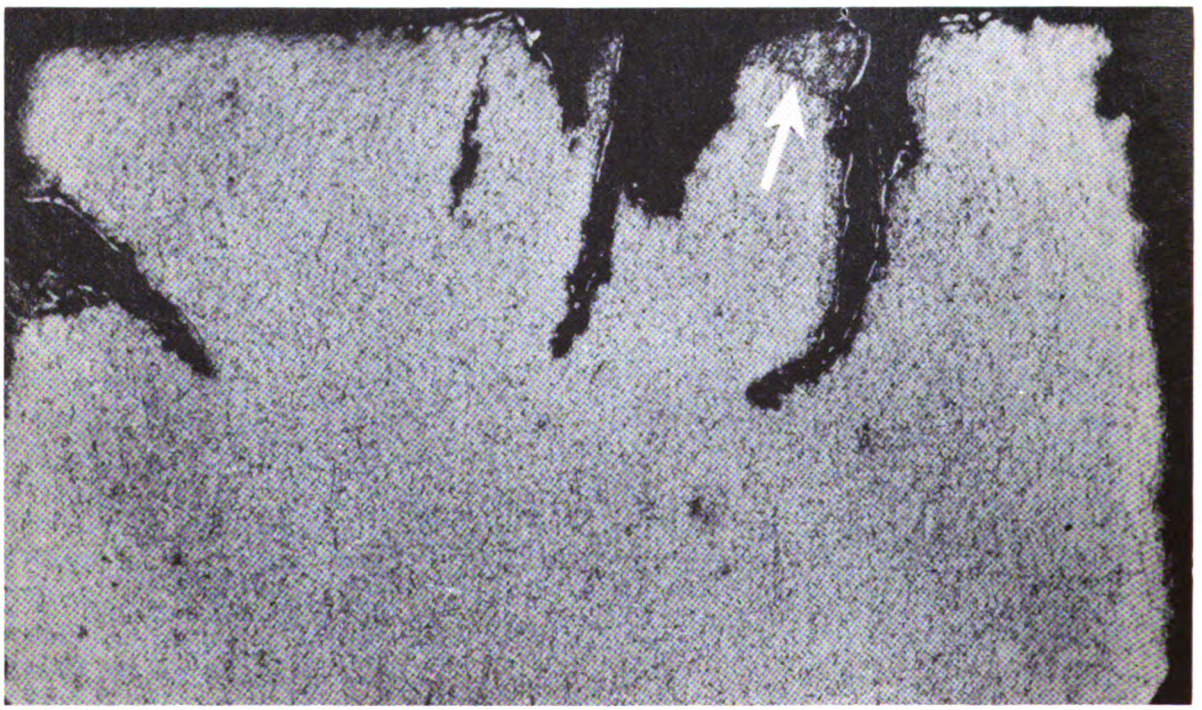


150X

Figure 23A. - Macrograph of section through sheared edge of series (a) sample.



150X

Figure 23B. - Macrograph of section through sheared edge of series (c) sample. Arrows indicate dark etching areas where the metal exceeded the transformation temperature (885° C.). Keller's etch.

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and (c) material, respectively, showing in section the depth of gullying at sheared edges and the hard, light etching oxidized spatter. The dark etching areas, indicated by the arrows, show that during the explosion the metal here was heated above the transformation temperature, that is, 885° C. The heat emitted from oxidation of the corroded material must therefore have been considerable. In figure 16 spatter from the sheared edge of an overlying sample is seen to outline the region of overlap. Figure 24 is a section through a similarly spattered area. It is observed that the heat emitted by the spatter material was sufficient to anneal the underlying worked metal to a depth of 0.002 inch. The sheared edges of series (d) samples underwent severe intergranular attack without any ignition of the corroded material. Figure 25 shows a sectional view through a sheared edge of a sample in this series.

Since the stress-corrosion attack at unannealed sheared edges figured so prominently in the explosion, it is of interest to illustrate in profile the texture and severity of deformation of an unsupported and supported sheared edge (note figs. 26 and 27, respectively).

Analytical Determination of Impurities

Several lots of commercial-grade titanium sheet were used in preparing test samples for RFNA corrosion studies. The analysis of these sheets is presented in table 2 for further reference.

TABLE 2

Source	Impurity, percent				
	Fe	C	N	Mg	Mn
Manufacturer B					
Sheet 1	0.14	0.056	0.028	0.005	0.079
Sheet 2 (series d & e)	.14	.064	.028	.005	.081
Sheet 3	.15	.044	.028	.005	.082
Manufacturer A - lot 1	.21	.043	.018	.005	.01
Manufacturer A - lot 2					
Hot-rolled (series c)	.39	.221	.019	.005	.024
10 percent cold-rolled[1]	.40	.196	.017	.005	.023
20 percent cold-rolled[1]	.39	.200	.016	.005	.024
30 percent cold-rolled[1]	.42	.206	.017	.005	.022
40 percent cold-rolled[1]	.41	.203	.017	.005	.022
50 percent cold-rolled[1]	.39	.179	.018	.005	.022

1/ Series a and b.

It is noteworthy that, in the earlier runs made by the corrosion lab with RFNA, sheets 1, 2, and 3, from manufacturer B, and lot 1, from manufacturer A, were used without mishap, even though severe intergranular corrosion occurred. The sample edges were sheared and spot welds prepared in a manner similar to that employed in the explosion run. Series (d) and (e) samples of the explosion run were cut from stock from manufacturer B. These samples likewise showed attack but no ignition. The sample series (a), (b), and (c) cut from lot 2, manufacturer A, were therefore the only commercial-grade titanium to be rendered pyrophoric on exposure to RFNA.

It is observed from table 2 that lot 2, manufacturer A, shows a significantly higher iron and carbon content that the other two.

Iron is soluble in alpha titanium to 0.1 percent; the balance is present in a metastable secondary phase of beta titanium. This iron-rich phase is seen in the

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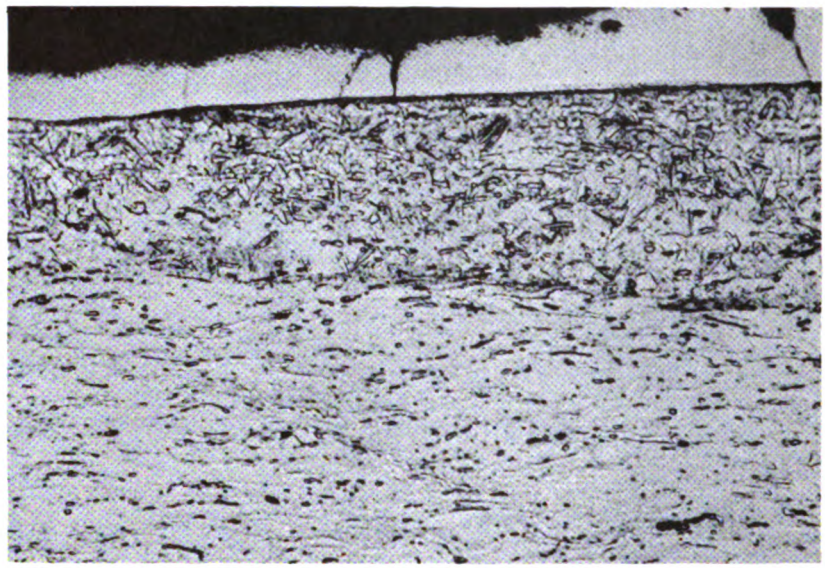
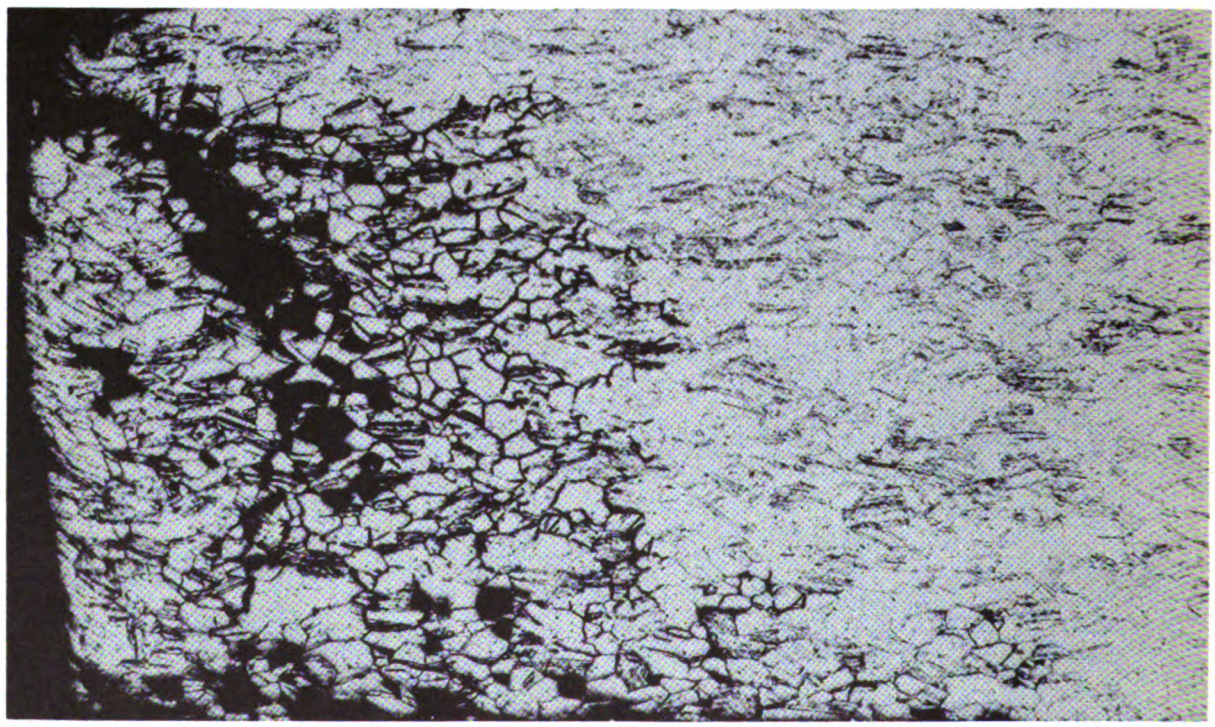


500X

Figure 24. - Section through spattered surface area similar to that seen in figure 16. Top light etching area is spatter material. Heat affected zone varies with the thickness of the spatter. Keller's etch.



100X

Figure 25. - Sectional view through sheared edge of a series (d) cold-rolled sample. Ignition of intergranularly corroded material is not observed. Keller's etch.

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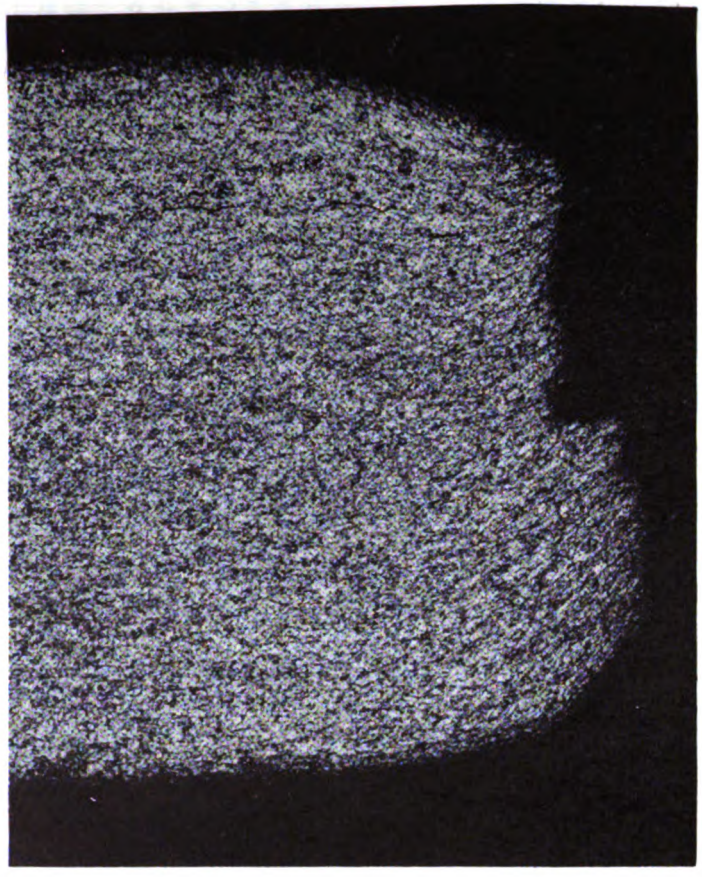

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Figure 26. - Profile of unsupported sheared edge, illustrating severity of deformation. Keller's etch.

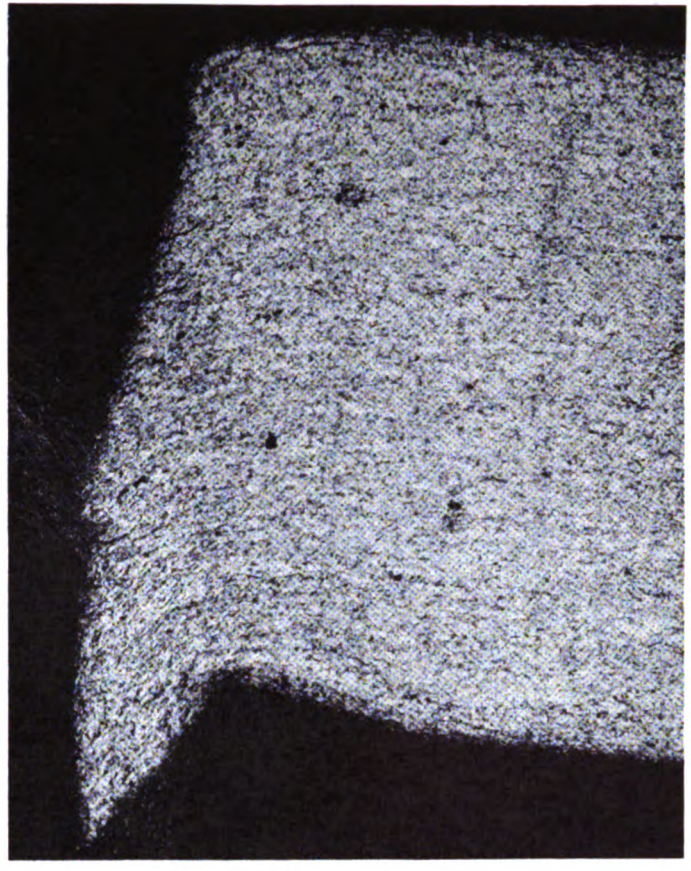

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Figure 27. - Profile of supported sheared edge, illustrating severity of deformation. Keller's etch.

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micrograph of the series (a) sample, figure 22, as fine globules concentrated largely at grain boundaries. Intergranular attack observed in this figure resulted in removal of the globular phase to the extent that a lower iron content would be anticipated in the attacked unignited surface areas of the series (a), (b), and (c) (high iron content) samples. To further this point, X-ray analyses were made of the surface layers of pitted unignited samples in the (a), (b), and (e) series with the following results:

Sample	Surface condition	Fe
Series (a), No. 20H	13 percent of surface pitted	0.32
	base metal[1/]	.37
Series (b), No. 50T	90 percent of surface pitted	.17
	base metal[1/]	.39
Series (e), No. Y	90 percent of surface pitted	.10
	base metal[1/]	.11

1/ Corrosion products were ground from the opposite sample surface and the base metal analyzed for Fe by X-ray spectroscopy.

Since X-ray spectroscopy averages the iron content in the top thousanths of an inch or so in a one-half inch square of surface area, it is apparent here in the (a) and (b) series samples that the iron content in the surface layers is reduced in proportion to the area attacked. Confirmatory data were obtained here on other samples. It follows that the intergranular corrosion accompanying pitting attacked the iron-rich phase concentrated at the grain boundaries in the (a) and (b) series samples and reduced the surface iron content. Likewise, since the iron content in the series (e) samples was largely in solution, it was not significantly reduced by intergranular attack. Although high iron content in the (a), (b), and (c) samples may conceivably have accelerated corrosion by providing avenues of attack in the form of an iron-rich grain broundary phase, it is presumptuous to state, with the evidence at hand, that high iron content necessarily rendered the corrosion products pyrophoric.

The carbon content of the corrosion products of the series (b) samples was determined colorimetrically from surface scrapings of attacked unignited areas to be 2- or perhaps 3-fold that of the base-metal content of 0.20 percent C. A carbon combustion analysis was made from millings cut from the ignited sheared edges of several series (a) samples, note figures 23A and B to a depth of 0.015 inch. Unfortunately, a large portion of base metal was included in the millings along with the corrosion products. Nevertheless, a carbon increase was obtained here also; 0.245 percent C, as compared with a base-metal content of 0.196 percent C. A carbon combustion analysis was also made on the intergranular corrosion products of an earlier run on manufacturer B's material exposed to RFNA in which corrosion products did not ignite. Figure 18 is a macrograph of a transverse section of a sample from this earlier run. Cuttings 1 mm. thick from the sheared edges of these samples analyzed 0.152 percent C, as compared to a base metal value of 0.044 percent C. It is thus concluded that the carbon impurity was attacked less than the titanium in the intergranularly corroded areas. Although the carbon was not depleted in the corrosion products as was the iron, there is no reason to exclude the function of the carbon as a possible catalyst in promoting the explosion.

Nitrogen, the third impurity analyzed in the explosion products, showed no significant change over the base-metal value. This element was also analyzed from sheared-edge cuttings taken from samples of the early RFNA run, illustrated in figure 18. The intergranularly corroded cuttings analyzed 0.031 percent N, as

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compared with the base-metal content of 0.028 percent N, the difference here being small.

Discussion

A staining type of surface attack, observed in the cold-rolled samples, series (d), was found to indicate extensive subsurface intergranular attack resulting in general embrittlement. Staining accompanied by intergranular corrosion was also observed in earlier RFNA tests on the same heat of titanium metal; no ignition of disintegrated material has been noted to date in this type of attack. Contrary to this, the cold-rolled samples, series (a), showed a pitting type of attack. Pitting in these samples did not exceed 14 percent of the surface area; maximum attack occurred between 20 and 30 percent cold roll. To the extent of the run there is an indication that a critical deformation exists in the 20 to 30 percent cold-rolling range to favor maximum pitting attack. Ignition of the pitted areas of the cold-rolled samples was light and did not involve over 2 percent of the surface pits.

Both the annealed series, (b) and (e), samples showed an equal degree of surface pitting, that is, covering approximately 50 percent of the surface area; neither series showed stress-corrosion attack, thus indicating complete stress relief. Although over 50 percent of the pitted area in the series (b) samples ignited during the explosion, showing a high degree of oxidation, none of the series (e) samples ignited.

It is considered that the dissimilarities noted above in the nature of the surface attack in the cold-rolled material from manufacturers A and B and the failure of any of the corroded material in the samples from manufacturer B to ignite during the explosion may be attributed in part to chemical differences in the two materials. The carbon and iron content of lot 2, manufacturer A (0.40 percent Fe, 0.20 percent C), ran about threefold that of lot from manufacture B (0.14 percent Fe, 0.064 percent C). It may be noted here that the ASTM Tentative Specification B265-52T for unalloyed titanium sheet limits the iron content to 0.25 percent maximum. Analytical results show that in the unignited corroded material the percentage carbon increased, the percentage nitrogen remained essentially unchaged, and the percentage iron was depleted; however, the procedure and outcome of the test in question did not permit definitely establishing the fact that either iron or carbon contributed to a sensitive pyrophoric condition.

Stress-corrosion attack observed in the test samples under question followed the direction of stress. In spot welds, the stress-corrosion cracking followed the periphery of the indentation and generally extended through the thickness of the sheet. A few of the samples had rolled edges, that is, edges of the original as-rolled sheet. Rolling sets up transverse fissures at the rolled edge, which act as stress raisers. Transverse corrosion cracking from this stress source was observed to propagate as far as 0.1 inch in from the sample edge. Shearing stresses are largely longitudinal, depending, however, in degree and direction on the shear pattern. Attack at sheared edges extended to a depth of 0.01 inch. Sheared-edge stress-corrosion attack was almost as extensive in the warm-rolled sample, (c) series with only 1 day exposure, as it was for the cold-rolled series (a) samples with 7.11 days exposure before the explosion. The fact that attack on the hot-rolled specimens was almost exclusively at the sheared edges and that the rate of attack was very high may be the result of electrochemical effects between the active metal at the sheared edges and the relatively inert oxidized surfaces. The attack on the cold-rolled specimens was concentrated at the edges to a small degree; this may have occurred because the oxide coating on the surfaces of these specimens was

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thinner and hence the difference of potential between the surfaces and the edges was smaller. Corrosion of vacuum-annealed specimens was more uniform because these differences may have been eliminated by stress relieving at 800° C. It has also been suggested that the attack on the edges of hot-rolled specimens appears to be unusually heavy because most of the corrosion at sheared edges normally takes place during the first day of immersion. However, there is no evidence for the theory that corrosion at the edges stops after 1 day.

Spatter was observed in all of the stress-corrosion areas of the material from manufacturer A. Spatter in the crevices of spot-weld cracking was infrequent, so that the heat liberated from this ignition would be minor. Attack at the rolled edges showed a moderate degree of spatter. However, since only a few of the samples had rolled edges, the heat evolved from oxidation of disintegrated material here did not contribute significantly to the total heat of the explosion. Spatter from the unannealed sheared edges of the material from manufacturer A was general and extensive.

It appears that the explosion was triggered by friction between samples created during venting one of the flasks. During the course of the explosion, a sudden rapid oxidation of the products of corrosion took place in some selected areas, with evolution of large amounts of heat. Where the heat was intense enough the products of oxidation fused (melted together) and were expelled. Although the oxidized pitted areas occupied considerable surface, they were too shallow to generate enough heat during oxidation to cause fusion. In the sheared edges, however, where stress had not been relieved by annealing, corrosion was deep, and the oxidation of disintegrated material generated enough heat to cause melting and spatter. Because of the evident loss of molten material at sheared edges, it is felt that these areas had more effect in causing the explosion than did the pitted flat surfaces.

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